Radical Polymerizations II
Special Cases

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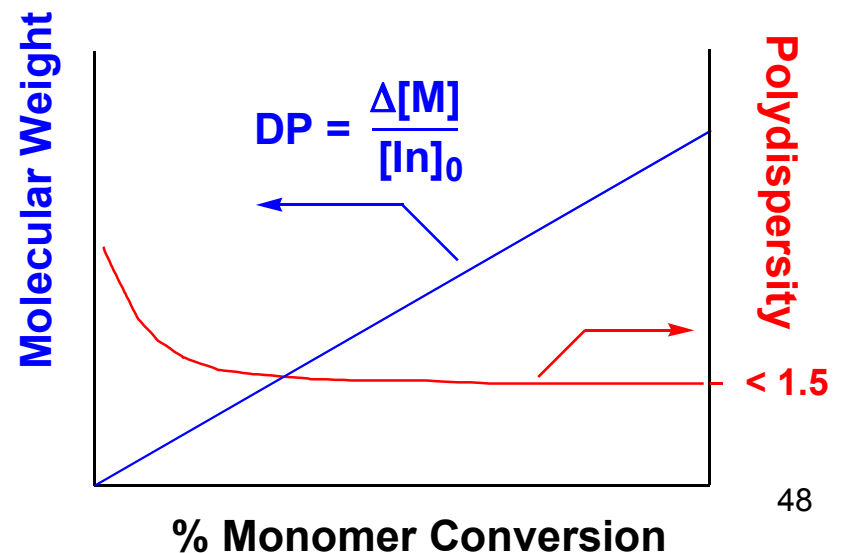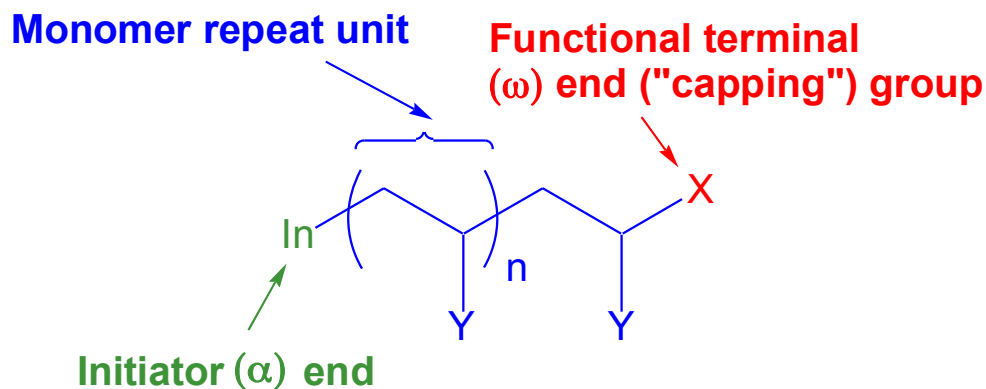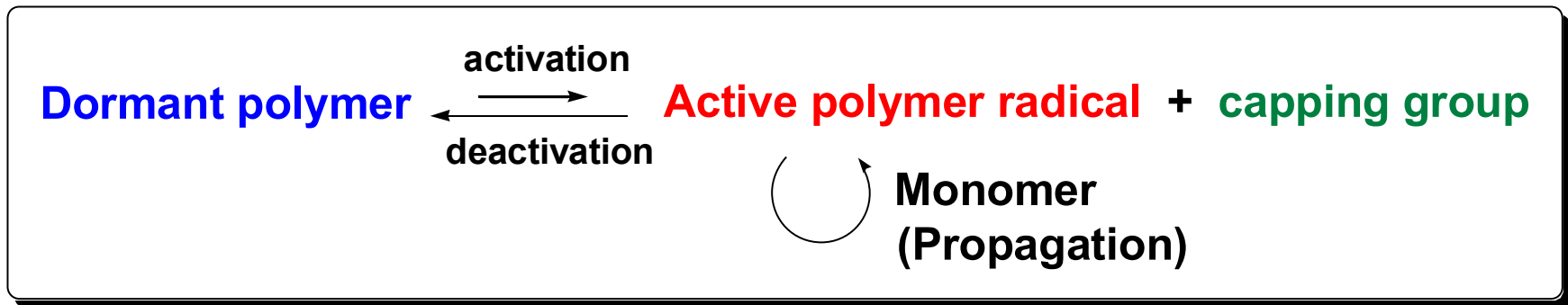Tel. (315) 268-2393, Fax (315) 268-6610

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defy convention ™

Living Polymerizations

- ## Objectives
  - ### Continuous chain growth
  - ### No termination
  - ### Well-defined chains
    - Chain structure
    - Chain length
    - Molecular weight distribution
    - Block copolymer synthesis

- ## Requirements
  - ### Initiation must be fast
    - $R_i \gg R_p$
  - ### Termination must be eliminated
    - Or at least reduced to insignificance

- ## Problems with free radical polymerization
  - ### Initiation is slow
  - ### Radical-radical termination is fast

Reversible-Deactivation Radical Polymerizations (RDRP)

- Often called *living radical polymerization*

Dormant polymer $\rightleftharpoons$ **Active polymer radical** + **capping group**

activation

deactivation

Monomer (Propagation)

Monomer repeat unit

Functional terminal (ω) end ("capping") group

In — [...]$_n$ — X

Y   Y

Initiator (α) end

Molecular Weight

$$DP = \frac{\Delta[M]}{[In]_0}$$

Polydispersity

< 1.5

% Monomer Conversion

Features of Living Polymerizations

- **Linear increase in molecular weight**
  - Vs. monomer conversion

- **Pre-defined molecular weight**
  - $DP_n = M_n/FW_M$
    $= \Delta[M] / [Initiator]$

- **Low polydispersity**
  - $M_w/M_n < 1.5$ (often ~ 1.1)

- **First-order monomer consumption**
  - Same as conventional radical polymerization

Terminology/Tests for Living Polymerization

- **Controversy over terminology**
  - Controlled, "living", pseudo-living, quasi-living, living/controlled, "living"/controlled, reversible-deactivation,…

- **IUPAC definition of "living polymerization":**
  - Absence of irreversible transfer and termination
    - Cannot be applied to any radical polymerization!

- **Some tests for RDRP:**
  - Continued chain growth after addition monomer added
  - Molecular weight increases linearly with conversion
  - Active species (i.e. radicals) conc. remains constant
  - Narrow molecular weight distributions (low M_w/M_n)
  - Block copolymers may be prepared (subset of first test)
  - End groups are retained – yields end-functionalized chains

Moad and Solomon *The Chemistry of Radical Polymerization*, 2nd edition, 2006, page 453.

Examples of RDRP Data

- **Atom transfer radical polymerization (ATRP)**
  - Styrene. M_n at 100% (theoretical) = 10,000 (DP = 100)
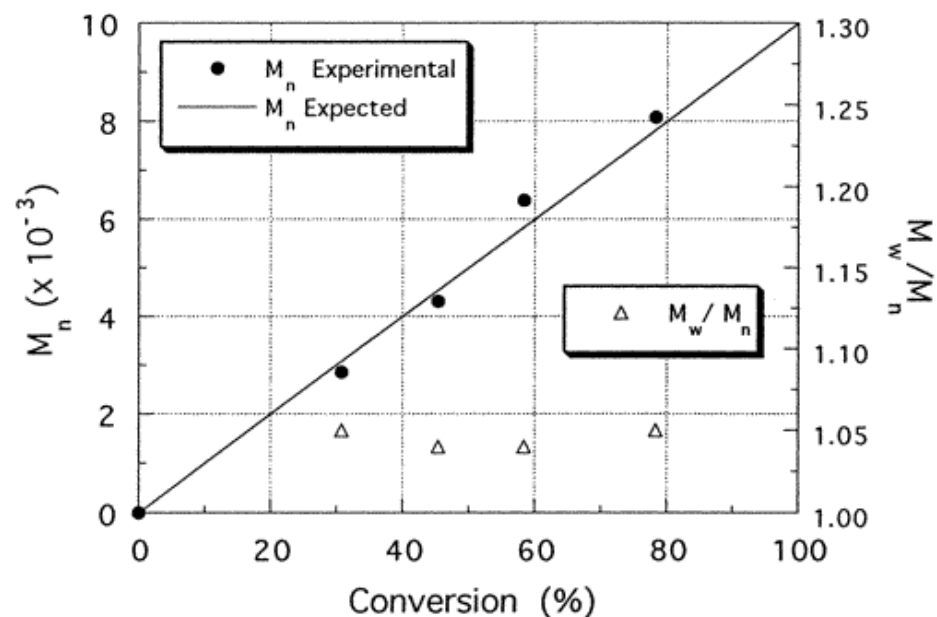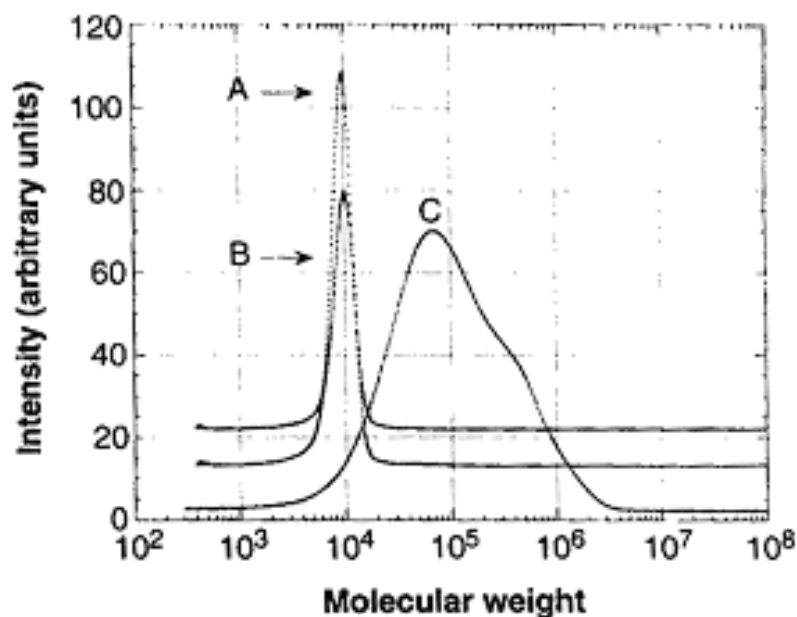
T.E. Patten, J. Xia, T. Abernathy, K. Matyjaszewski, *Science*, **1996**, *272*, 866.
K. Matyjaszewski, T.E. Patten, J. Xia, *J. Am. Chem. Soc.*, **1997**, *119*, 674.
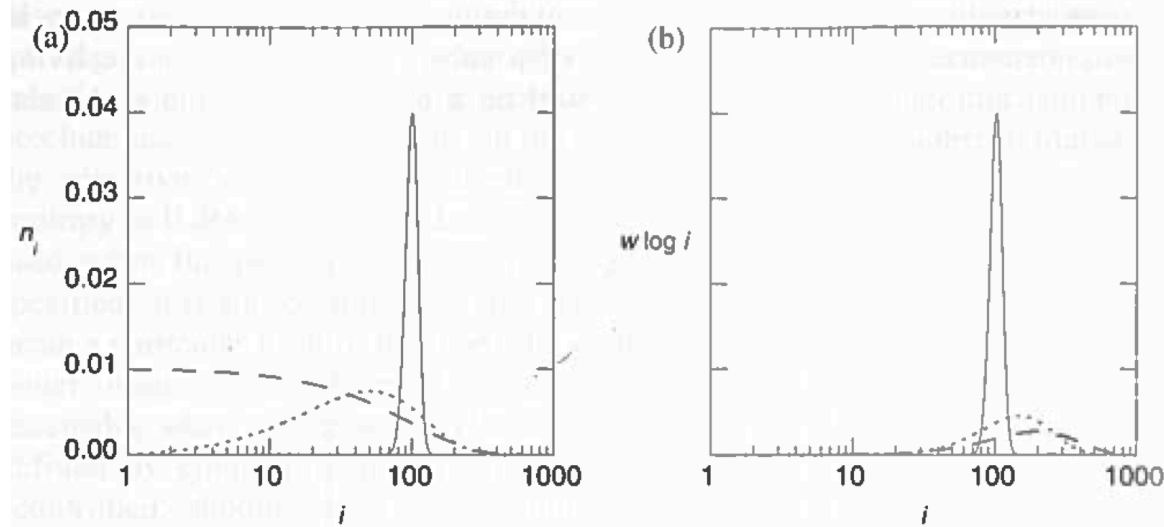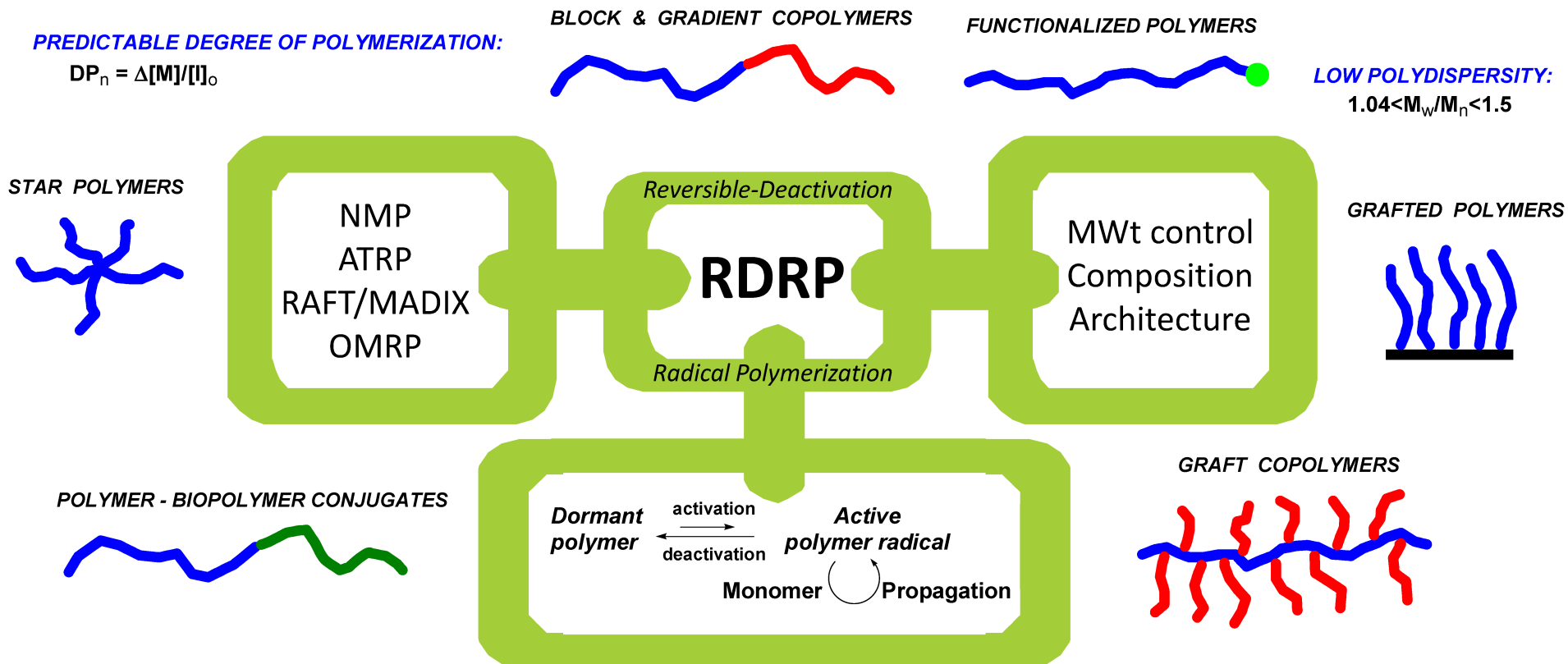
Calculated MWDs

Figure 9.2 Calculated (a) number and (b) GPC distributions for three polymers each with $\overline{X}_n$=100. The number distributions of chains formed by conventional radical polymerization with termination by disproportionation or chain transfer (– – –, $\sum n_i$=1.0, $\overline{X}_w / \overline{X}_n$=2.0) or termination by combination (------, $\sum n_i$=1.0, $\overline{X}_w / \overline{X}_n$=1.5) were calculated as discussed in Section 5.2.1.3. The number distribution of chains formed in an ideal living polymerization (——, $\sum n_i$=1.0, $\overline{X}_w / \overline{X}_n$=1.01) was calculated using a Poisson distribution function.

Moad and Solomon *The Chemistry of Radical Polymerization*, 2nd edition, 2006, page 454.

Materials From RDRP

PREDICTABLE DEGREE OF POLYMERIZATION:

$DP_n = \Delta[M]/[I]_o$

BLOCK & GRADIENT COPOLYMERS

FUNCTIONALIZED POLYMERS

LOW POLYDISPERSITY:

$1.04 < M_w/M_n < 1.5$

STAR POLYMERS

GRAFTED POLYMERS

NMP ATRP RAFT/MADIX OMRP

Reversible-Deactivation

RDRP

Radical Polymerization

MWt control Composition Architecture

POLYMER - BIOPOLYMER CONJUGATES

GRAFT COPOLYMERS

Dormant polymer ⇌ Active polymer radical

activation

deactivation

Monomer ⟳ Propagation

D.A. Shipp, *Polym. Rev.*, **2011**, *51*, 99-103.

RDRP: Types & Requirements

- **Main types**
  - Nitroxide-Mediated Polymerization
    - NMP
  - Atom Transfer Radical Polymerization
    - ATRP
  - Reversible Addition-Fragmentation Chain Transfer Polymerization
    - RAFT

- **Other types**
  - Metal-mediated polym'n
  - Iniferter
  - Group transfer polym'n

- **Requirements**
  - All chains begin at the same time
    - "Fast initiation"
  - Little or no termination
    - Low radical concentration
  - All chains grow at the same rate
    - "Fast exchange"

  - Iodo and methacrylate-based degenerate transfer

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Nitroxide-Mediated Polymerization

- ## Nitroxides
  - Stable free radicals
  - Do not react with O-centered radicals
  - React fast with C-centered radicals
    - $k_d \sim 10^6 - 10^9$ M^{-1} s^{-1}
  - Do not initiate polymerization

P_n-X $\underset{k_d}{\overset{k_a}{\rightleftharpoons}}$ $P_n^{\bullet}$ + X$^{\bullet}$

k_p
Monomer
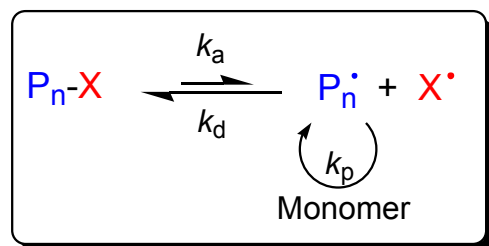
- ## TEMPO
  - 2,2,6,6 tetramethylpiperidim-N-oxyl
  - Only good for styrene (co)polymers
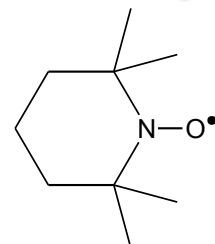
- ## α−H nitroxides
  - Styrene, acrylates, acrylonitrile, 1,3-butadiene
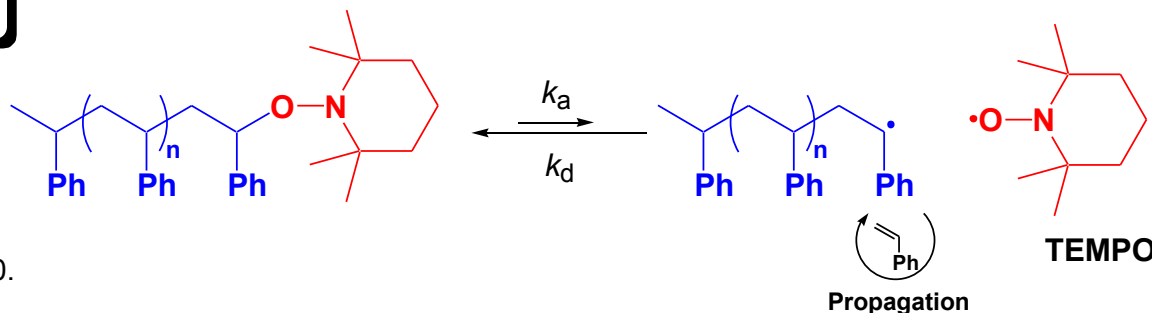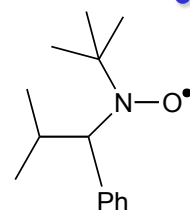
Rizzardo, Solomon, et al.
US Patent 4,581,429, **1986**.
Aust. J. Chem., **1990**, *43*, 1215-1230.
Chem. Aust., **1987**, *54*, 32.

Ph   Ph   Ph $\underset{k_d}{\overset{k_a}{\rightleftharpoons}}$ Ph   Ph   Ph

Propagation

TEMPO

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Georges/Xerox Approach to NMP
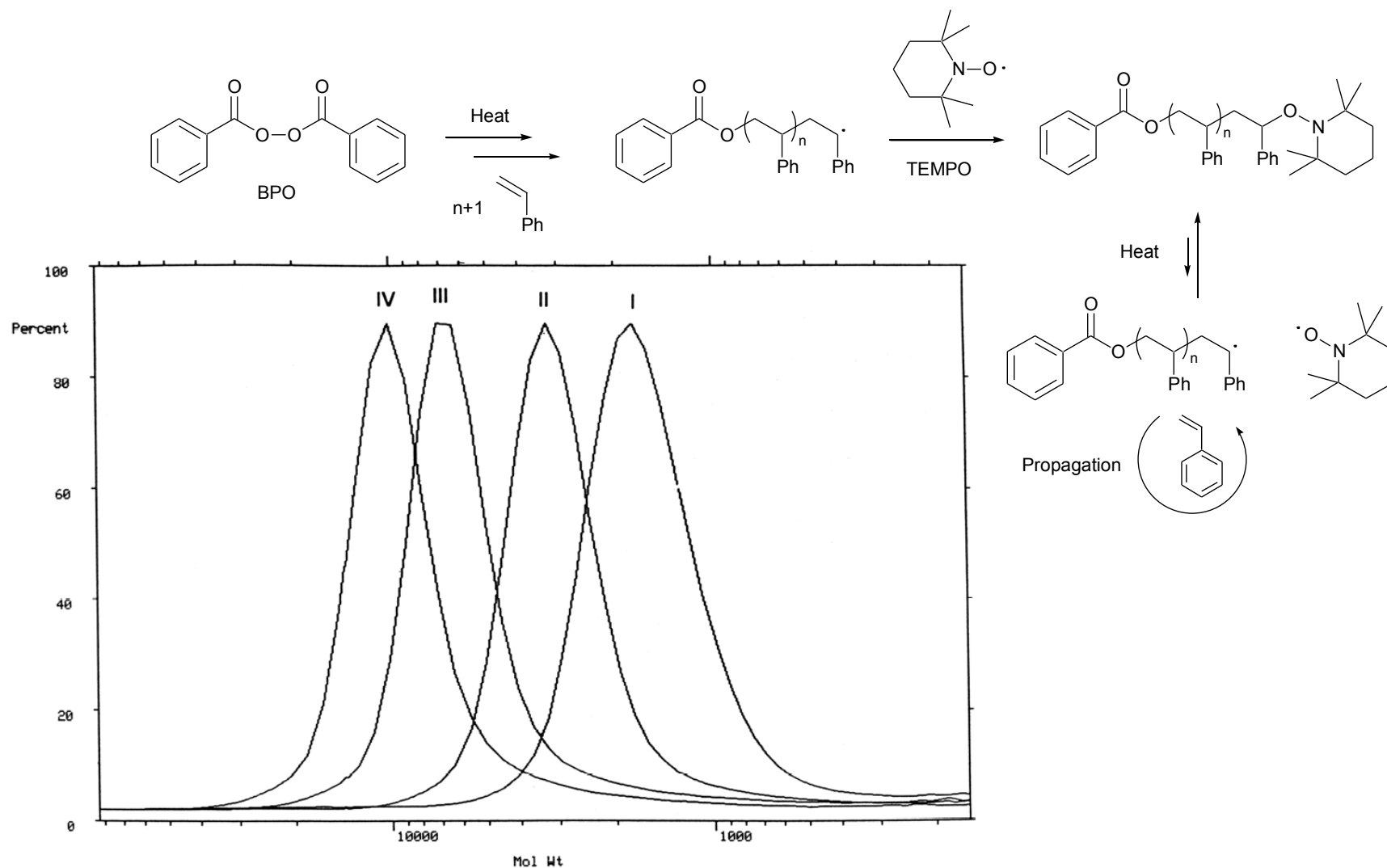
Molecular weight distributions of polystyrene produced by NMP using BPO and TEMPO. M_n and M_w/M_n of samples I – IV are as follows: ($M_n:M_w/M_n$) 1700:1.28, 3200:1.27, 6800:1.21, 7800:1.27.

M.K. Georges et al., *Macromolecules*, **1993**, *26*, 2987-2988.
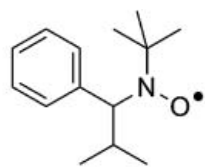
Hawker Approach to NMP (Using TEMPO)

Alkoxyamine

C.J. Hawker, *J. Am. Chem. Soc.*, **1994**, *116*, 11185-11186.
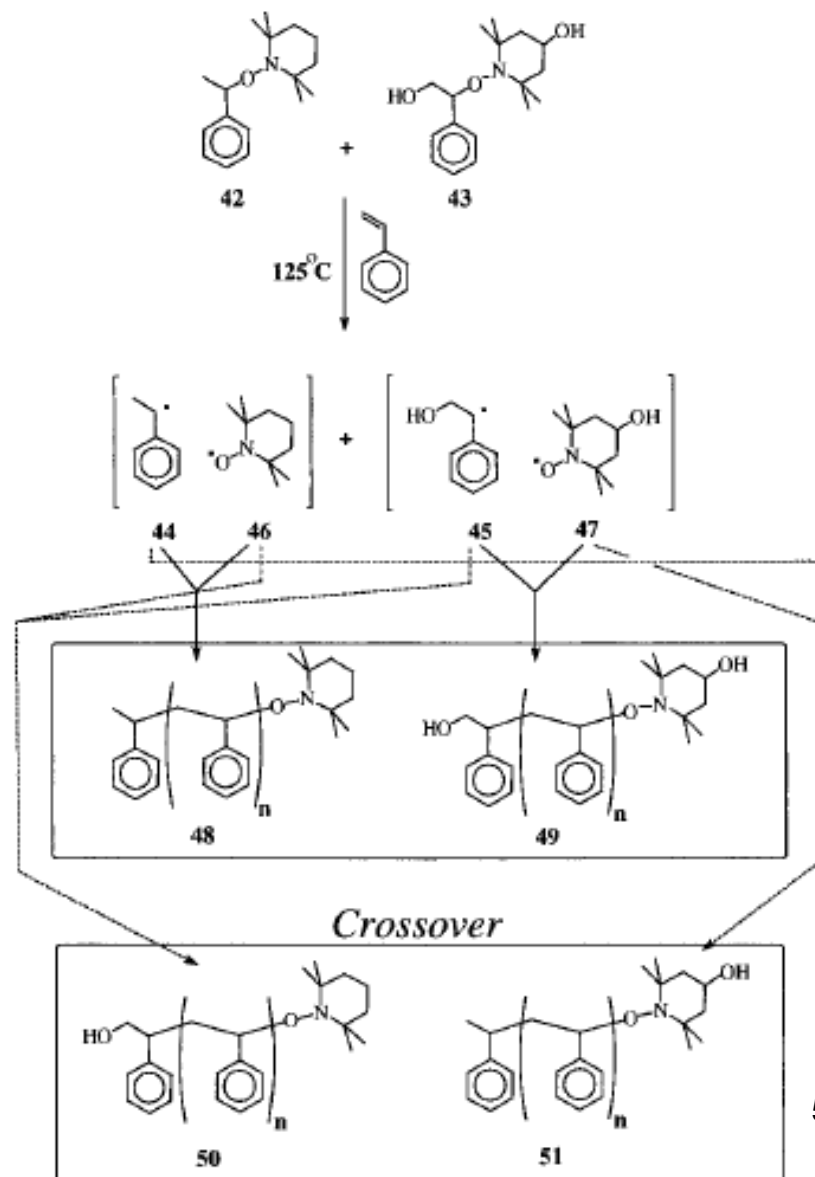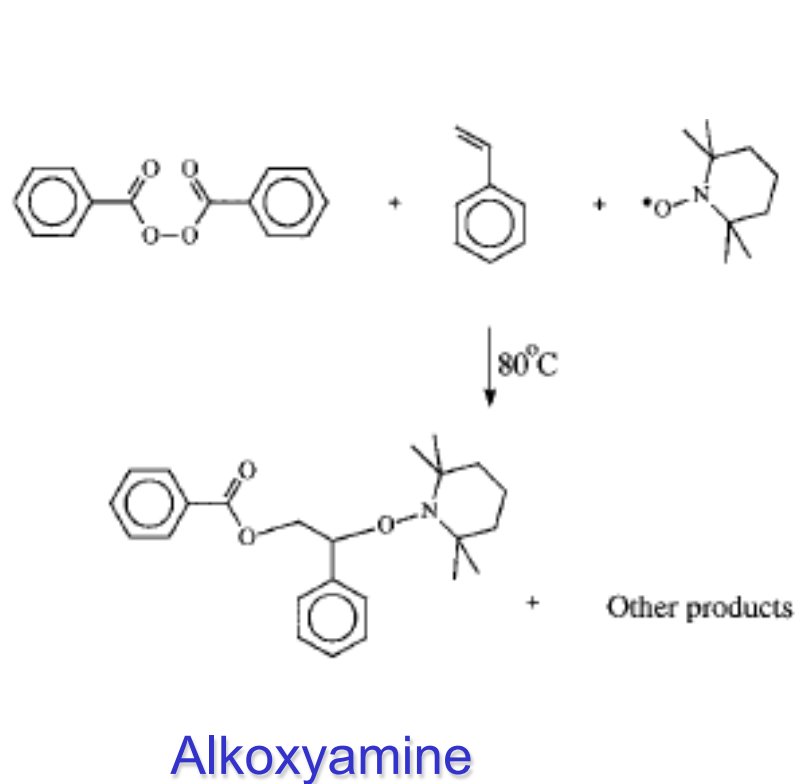
Newer Nitroxides: α-Hydrido-Derivatives

- ## Wider range of monomers & functionalities

Common nitroxides/alkoxyamines
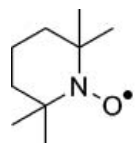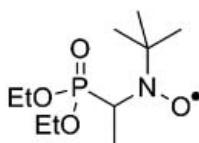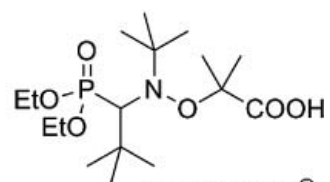
TEMPO   TIPNO   SG1   BlocBuilder® (MAMA-SG1)

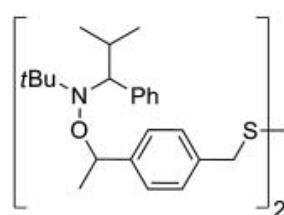Functional alkoxyamines
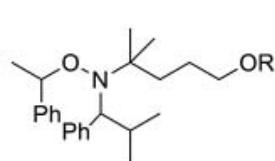
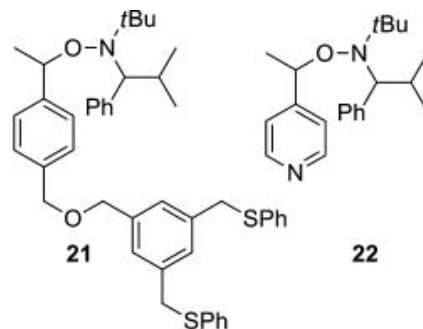17: R= -H
18: R= -CO(CH₂)₂CO₂H

19   20   21   22

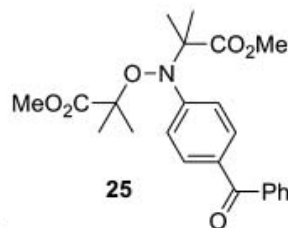23   25   26   27

24

P. Tordo, Y. Gnanau, et al., *J. Am. Chem. Soc.*, **2000**, *122*, 5929-5939.
C.J. Hawker, et al., *J. Am. Chem. Soc.*, **1999**, *121*, 3904-3920.

R.B. Grubbs, *Polym. Rev.*, **2011**, *51*, 104-137.
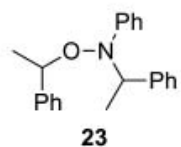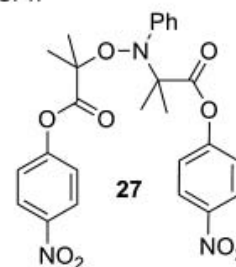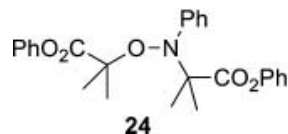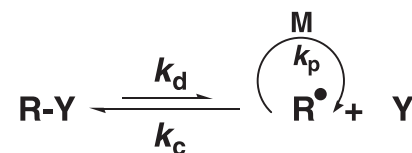
The Persistent Radical Effect (PRE)

- Idea developed by H. Fischer, and furthered by T. Fukuda

$$R\text{-}Y \underset{k_c}{\overset{k_d}{\rightleftharpoons}} R^\bullet + Y \quad (M, k_p)$$

Concentration: I   R   Y

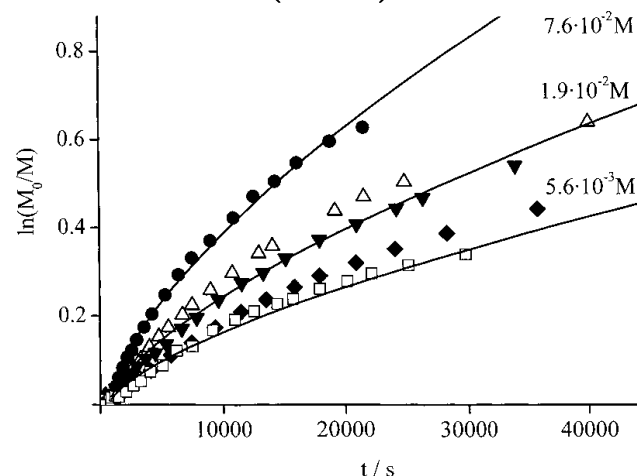$$R^\bullet + R^\bullet \xrightarrow{k_t} R\text{-}R + R\text{-}H/R^=$$
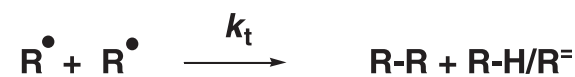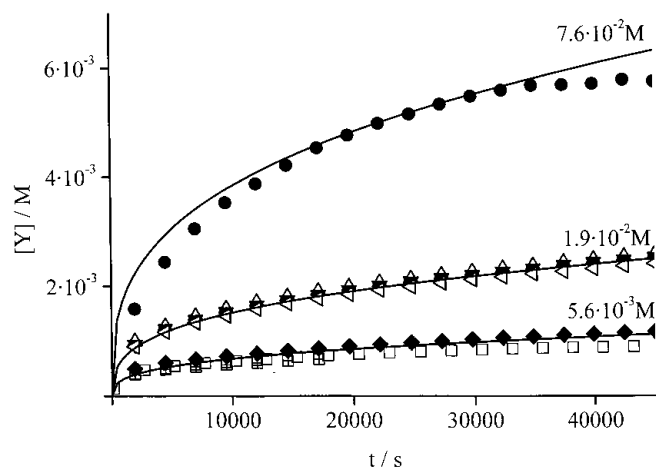
Concentration: R   R   P

$$\frac{dR}{dt} = k_d I - k_c RY - 2k_t R^2,$$

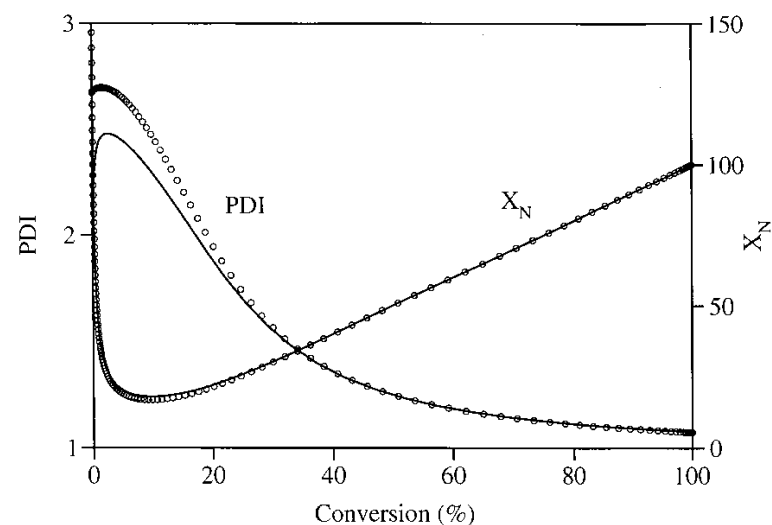$$\frac{dY}{dt} = k_d I - k_c RY = \frac{dR}{dt} + 2k_t R^2.$$

$$Y = (6k_t K_{eq}^2 I_0^2)^{1/3} t^{1/3},$$

$$R = \left(\frac{K_{eq} I_0}{6k_t}\right)^{1/3} t^{-1/3}.$$

Chem. Rev. **2001**, *101*, 3851-3610.

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Consequences of the PRE

- **Better control over polymer growth**
  - Faster deactivation

  - Fewer radicals
    - Slower termination ($R_t \sim [R\bullet]^2$)
    - Slower polymerization ($R_p \sim [R\bullet]$)
    - Better chain end functionalization

  - Odd polymerization kinetics
    - Approx. $t^{1/3}$ dependence instead of t

  - Can add some extra persistent radical (e.g. nitroxide) to improve PDI, slow rate, better end group control

Atom Transfer Radical Polymerization

Cu^IBr + [bipyridine ligand] or [triamine ligand]

Metal "catalyst" (& ligand, L)

Active propagating radical

$Cu^{II}Br_2$ + ligand

Oxidized metal "catalyst"

$$P_n\text{-}X + Mt^q/L \underset{k_d}{\overset{k_a}{\rightleftharpoons}} P_n{}^* + X\text{-}Mt^{q+1}/L$$

$$\downarrow k_p \quad \overset{P_m{}^*}{\searrow} k_t$$

Monomer → $D + 2\, X\text{-}Mt^{q+1}/L$

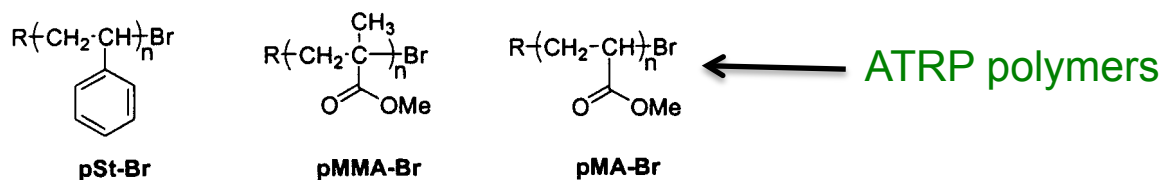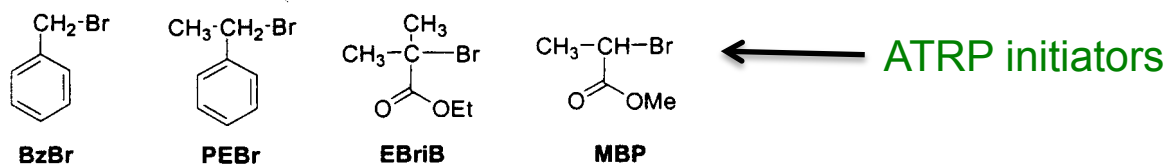**Dormant chain with halogen (X)**

"Dead" chains
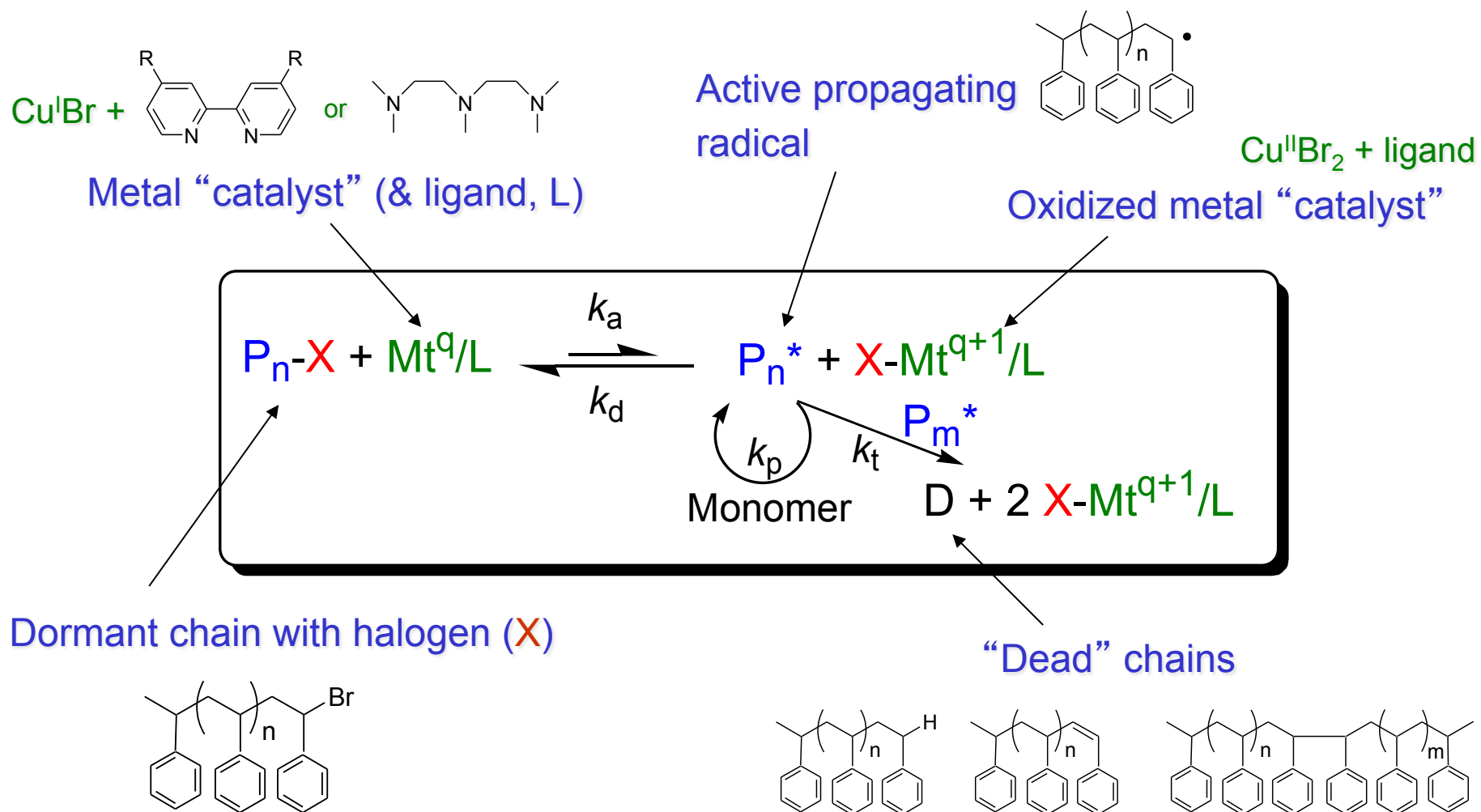
J.-S. Wang, K. Matyjaszewski, *J. Am. Chem. Soc.*, **1995**, *117*, 5614.
M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, *Macromolecules*, **1995**, *28*, 1721.
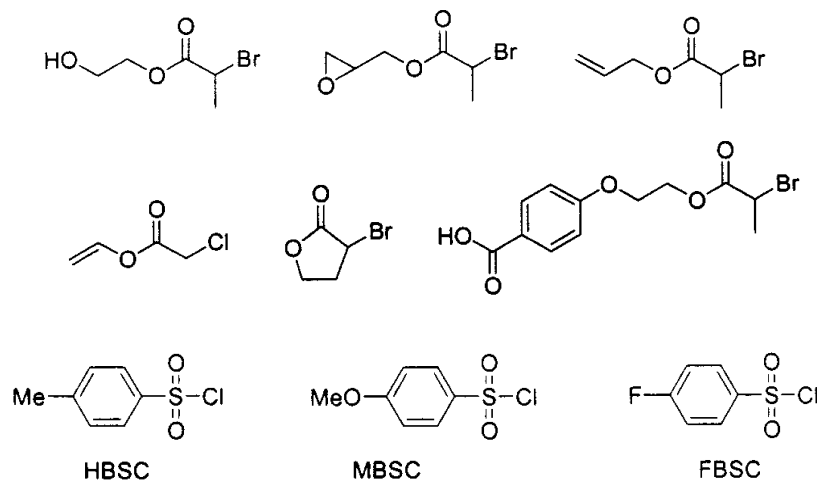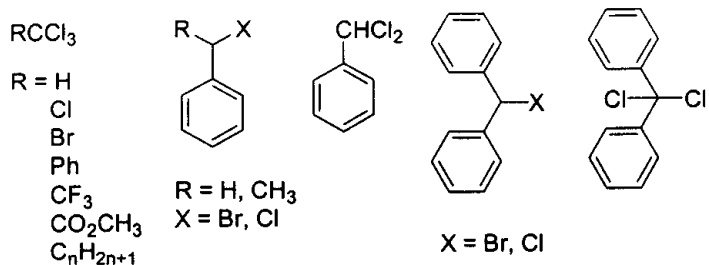V. Percec, B. Barboiu, *Macromolecules*, **1995**, *28*, 7970.

Initiators for ATRP

- Best to "copy" end of growing polymer

ATRP initiators

ATRP polymers

Other ATRP initiators used include:

K. Matyjaszewski, J. Xia, *Chem. Rev.* **2001**, *101*, 2921-2990.
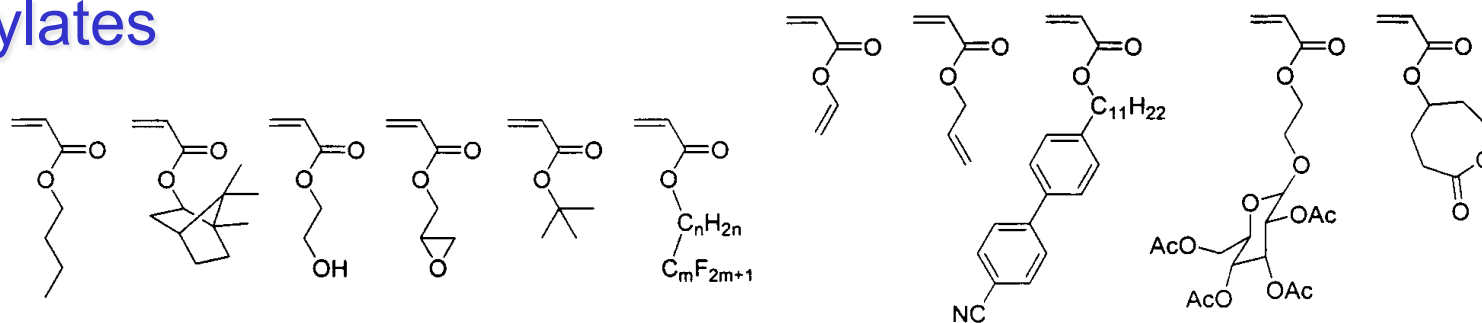
Monomers for ATRP

- **Styrenics**
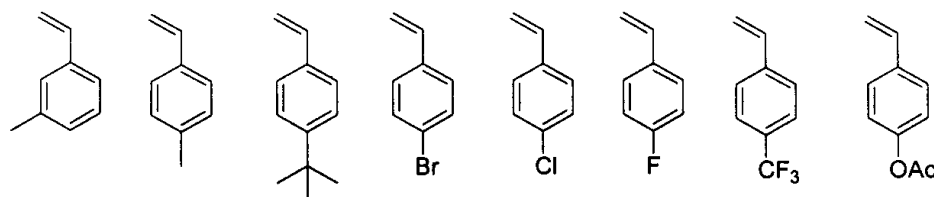
- **Acrylates**

- **Methacrylates**
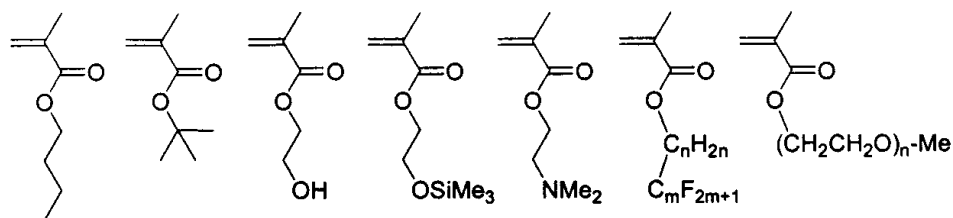
- Other monomers, such nitriles, can be polymerized.
- Nucleophilic functionalities (e.g., amines, acids) can cause problems.

K. Matyjaszewski, J. Xia, *Chem. Rev.* **2001**, *101*, 2921-2990.

Catalysts for ATRP

- ## Ru, Ni, Fe & Cu
  - ## Cu most used

Common ligands used with Cu

ATRP catalysts based on other metals

K. Matyjaszewski, J. Xia, *Chem. Rev.* **2001**, *101*, 2921-2990.

K. Matyjaszewski, N.V. Tsarevsky, *Nat. Chem.* **2009**, *1*, 276-288.
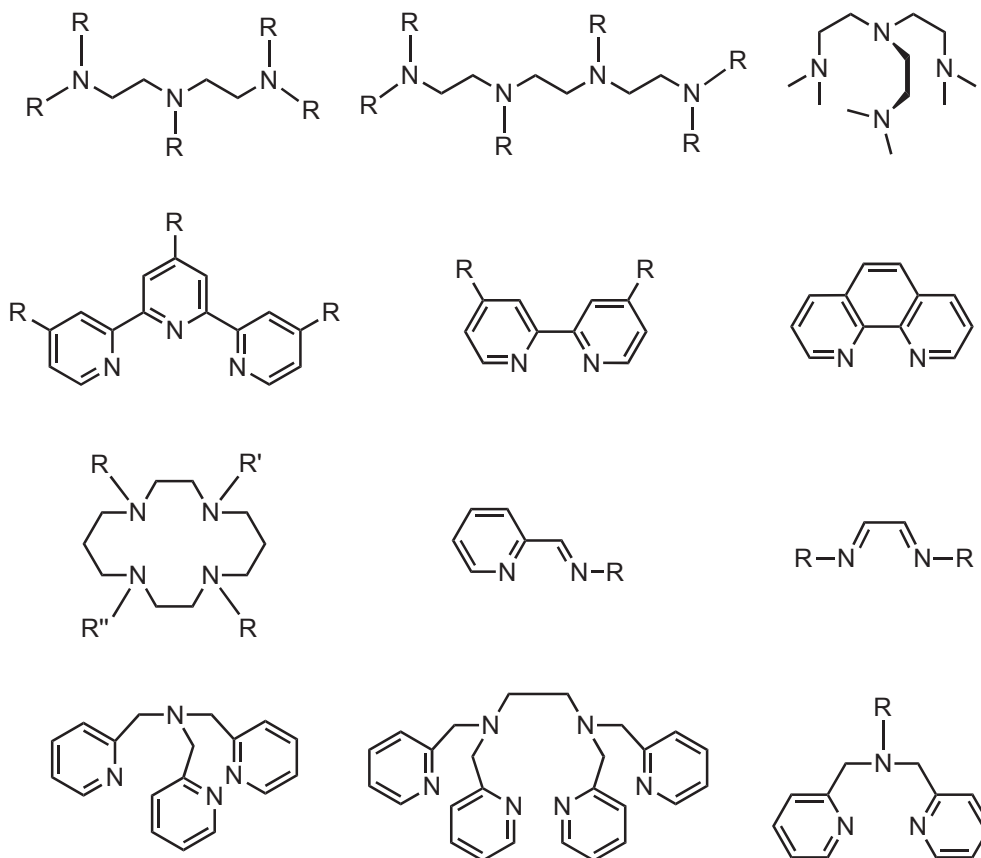
Functional Polymers by ATRP

End-group functionalization easy to perform with various alkyl halide reactions

K. Matyjaszewski, N.V. Tsarevsky, *Nat. Chem.* **2009**, *1*, 276-288.
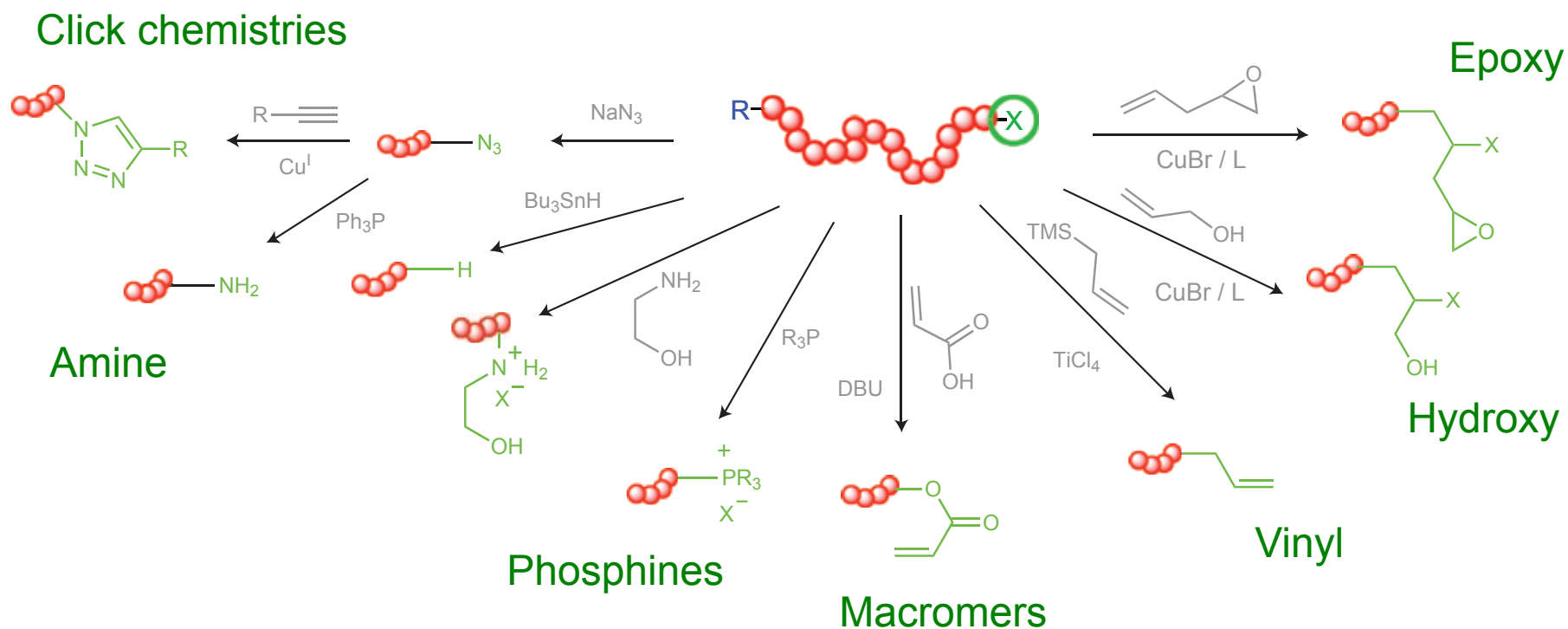
Some Mechanistic Details

- ## Halogen exchange

$$RBr + CuCl/L \; \underset{}{\overset{K_{exch}}{\rightleftharpoons}} \; RCl + CBr/L$$

BzX

1-PEX

MeBrP

Et-2-BriB

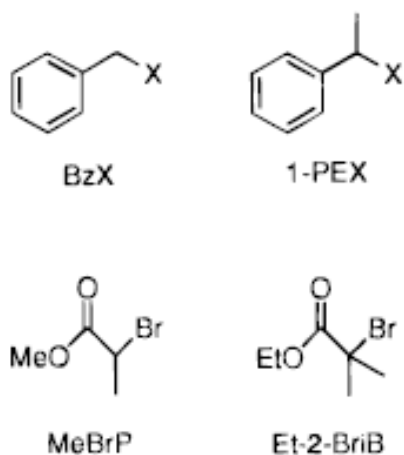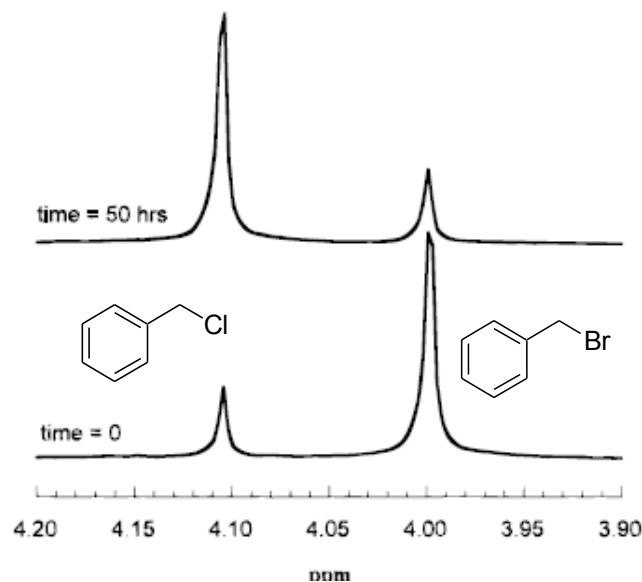Table 1. Percentage of R−Cl as a Function of Time in R−X/Cu−Y Halide Exchange Reactions As Monitored by Gas Chromatography (GC)[a]

system (R−X/Cu−Y)	10 min	25 min	40 min	90 min
BzBr/CuCl[b]	66	78	81	
BzCl/CuBr[b]	94	90	87	82
1-PEBr/CuCl[b]	87	91	91	
1-PECl/CuBr[b]		90	88	89
Et-2-BriB/CuCl[c]	91	91	91	
MeBrP/CuCl[c]	79	84	85	

Figure 1. ¹H NMR spectra obtained from the model study of BzBr/CuCl at room temperature at the times indicated (last entry in Table 2). [BzBr] = 0.1 M, [CuCl] = 0.1 M, [dNbpy] = 0.2 M solvent = benzene-d_6.

time = 50 hrs

time = 0

4.20   4.15   4.10   4.05   4.00   3.95   3.90

ppm

K. Matyjaszewski et al. *Macromolecules* **1998**, *31*, 6836-6840.

How to Utilize Halogen Exchange

- ## Better control of homopolymerizations

Figure 2. Dependence of molecular weights (filled symbols) and polydispersities (open symbols) of PMMA on monomer conversion for solution ATRP of MMA in diphenyl ether at 90 °C using BzCl/Cu^{I}X initiation systems, where X = Cl (○, ●) and Br (□, ■). Line is predicted molecular weight based on $M_n^{th} = 100.12(\Delta[M]/[In]_0)p$, where $[In]_0$ = initial initiator concentration and p = fractional conversion. $[BzCl]_0 = 0.021$ M, $[CuX]_0 = 0.011$ M, $[dNbpy] = 0.021$ M.
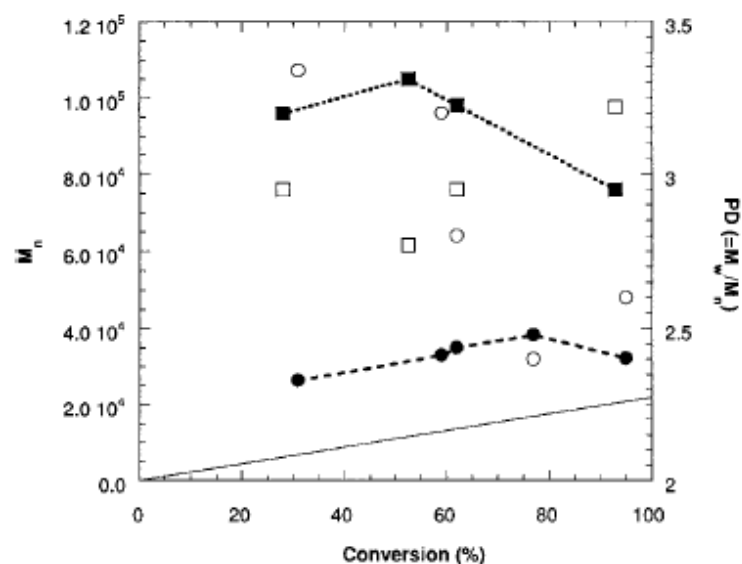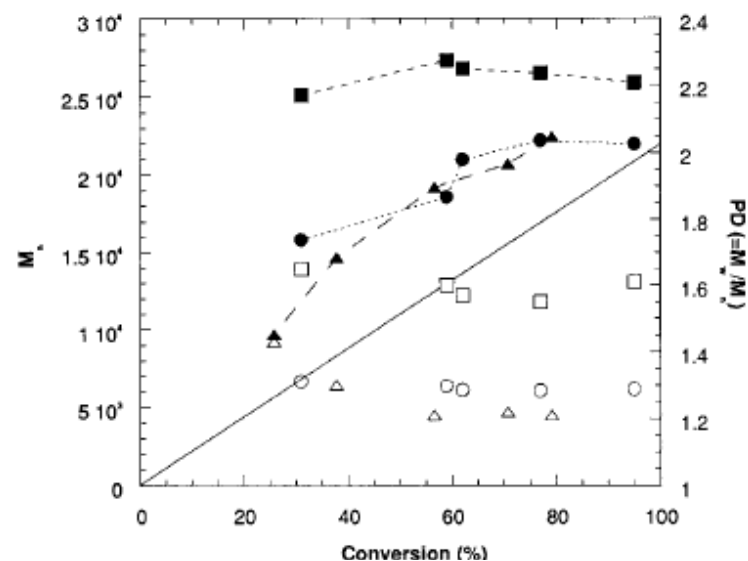
Figure 3. Dependence of molecular weights (filled symbols) and polydispersities (open symbols) of PMMA on monomer conversion for solution ATRP of MMA in diphenyl ether at 90 °C using BzBr/Cu^{I}X initiation systems, where X = Cl (○, ●, △, ▲) and Br (□, ■). Line is predicted molecular weight based on $M_n^{th} = 100.12(\Delta[M]/[In]_0)p$, where $[In]_0$ = initial initiator concentration and p = fractional conversion. For (○, ●, □, ■), $[BzBr]_0 = 0.021$ M, $[CuX]_0 = 0.011$ M, $[dNbpy] = 0.021$ M; for (△, ▲), $[BzBr]_0 = 0.021$ M, $[CuCl]_0 = 0.021$ M, $[dNbpy] = 0.042$ M.

K. Matyjaszewski et al. *Macromolecules* **1998**, *31*, 6836-6840.

Utilizing Halogen Exchange...2
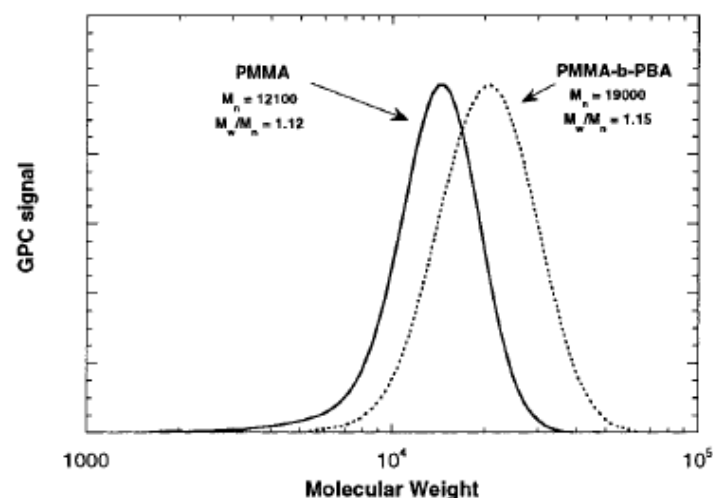
- ## Better block copolymers

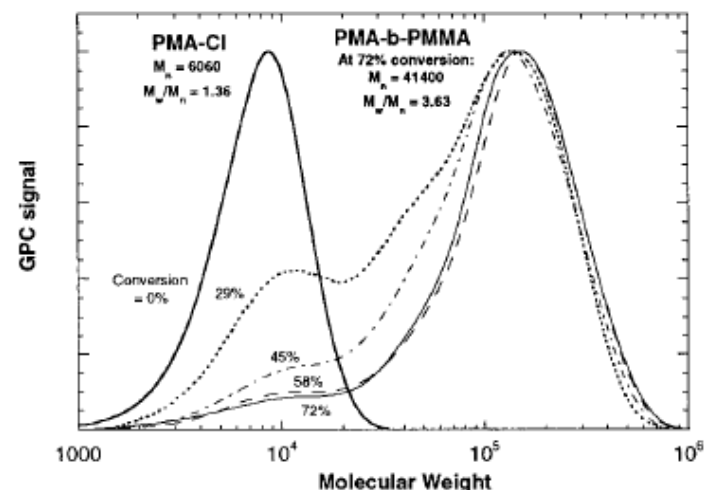Figure 1. Molecular weight distributions of PMMA macro-initiator and PMMA-*b*-PBA diblock copolymer.

Figure 3. Molecular weight distributions of PMA-Cl macro-initiator and PMA-*b*-PMMA diblock copolymer at various monomer conversions (indicated in the figure).
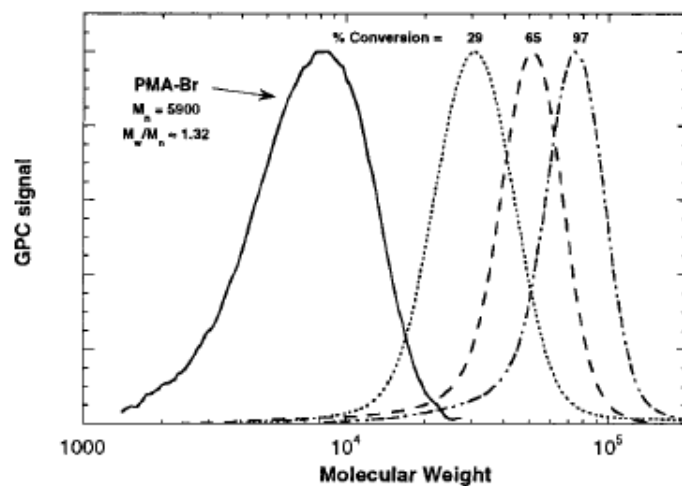
Figure 6. Molecular weight distributions of PMA-Br macro-initiator and PMA-*b*-PMMA diblock copolymer at various monomer conversions.

D.A. Shipp, J.-L. Wang, K. Matyjaszewski
Macromolecules **1998**, *31*, 8005-8008.

"Reverse" ATRP

- Add regular initiator (e.g. AIBN), with oxidized metal (e.g. $Cu^{II}Br_2$) & ligand
  - Less trouble handling Cu^{II} (c.f. Cu^{I})
  - Uses common initiator
  - Still provides good control, etc.
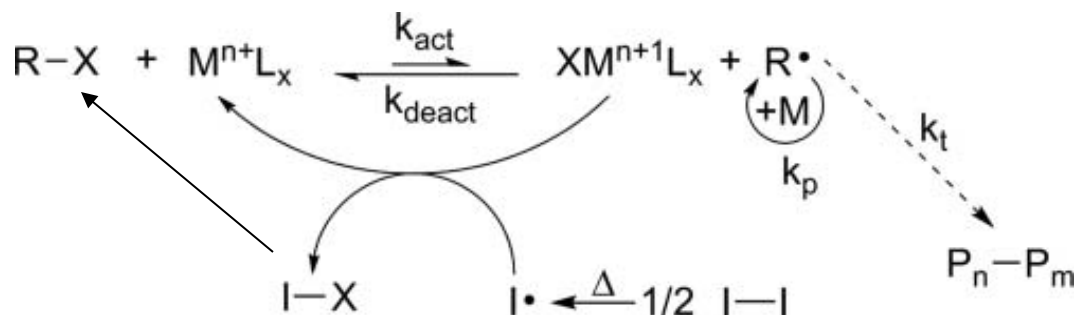
- Related to "ICAR" ATRP
  - Initiators for continuous activator regeneration
  - Allows for lower Cu concentrations

J.-S. Wang, K. Matyjaszewski *Macromolecules*, **1995**, *28*, 7572-7573.
K. Matyjaszewski et al. *Proc. Natl. Acad. Sci. U.S.A.*, **2006**, *103*, 15309-15314.

Activator (Re)Generated by Electron Transfer (AGET & ARGET) ATRP

- **Problem: use of Cu metal salts contaminates polymer**
  - Usually ends up being green
  - Adds expense to polymerization

- **Overcome this by regenerating Cu(I) by using a reducing agent such as amines, glucose, ascorbic acid, etc., as well as Cu(0) wire**
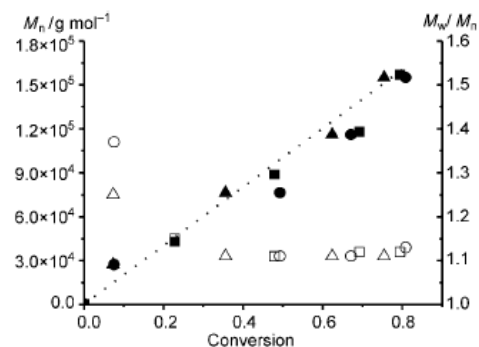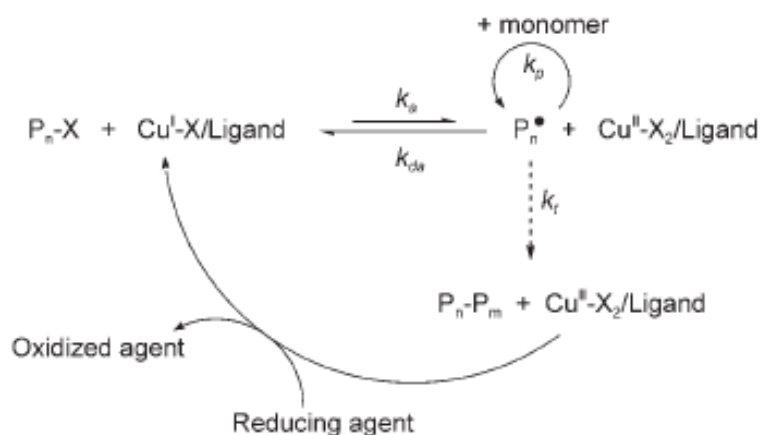 - Much lower [Cu]

$$P_n\text{-}X + Cu^I\text{-}X/Ligand \underset{k_{da}}{\overset{k_a}{\rightleftarrows}} P_n^\bullet + Cu^{II}\text{-}X_2/Ligand$$

with + monomer (k_p), and k_t leading to $P_n\text{-}P_m + Cu^{II}\text{-}X_2/Ligand$

Oxidized agent / Reducing agent

Figure 3. Plot of M_n (filled shapes) and M_w/M_n (empty shapes) versus conversion for three consecutive polymerizations of MMA with CDB using the same copper wire as the reducing agent. 1st use ●, ○, 2nd use ■, □, 3rd use ▲, △. Polymerization conditions: $[MMA]_0/[CDB]_0/[CuBr]_0/[TPMA]_0 = 2000:1:0.01:0.03$; MMA/anisole $= 1:2$ (v/v); 72 h at 80 °C; copper(0) wire $l = 70$ cm, $d = 1$ mm.

K. Matyjaszewski et al. *Angew. Chem. Int. Ed.* **2010**, *49*, 541-544.
Chem. Rev. **2007**, *107*, 2270-2299

SARA ATRP vs. SET LRP

- ## Controversy over ARGET-type approach
  - ### SARA = supplemental regeneration of activators
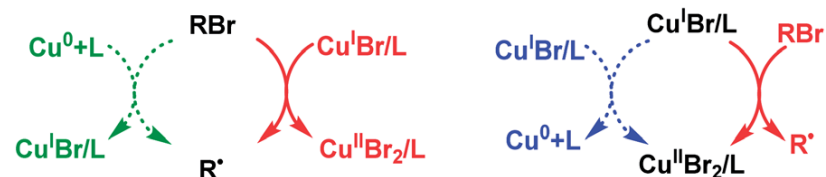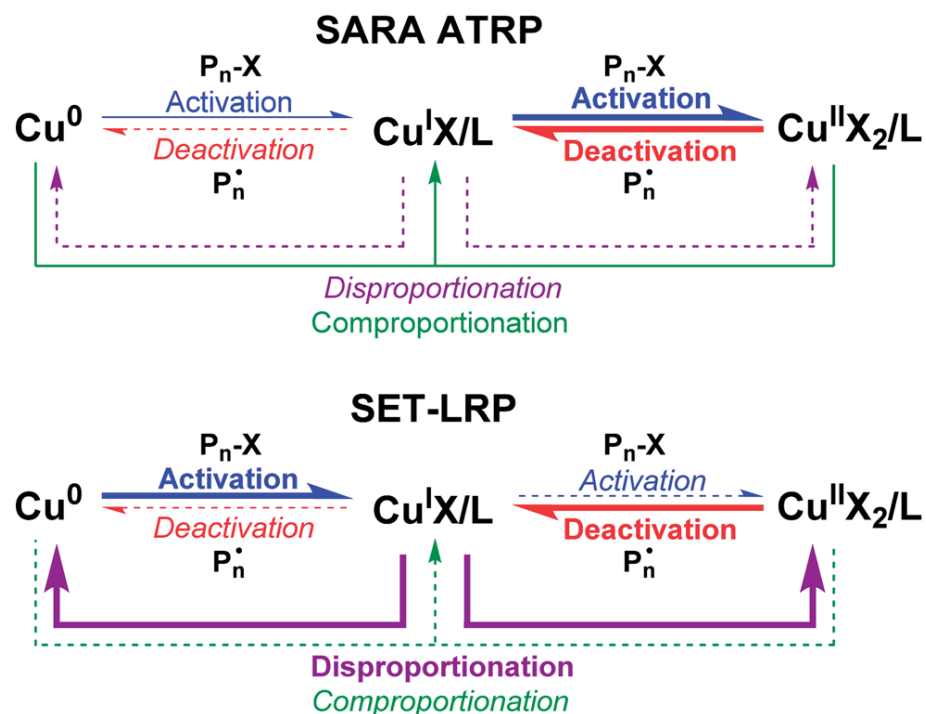
Scheme 2 Key differences between the SARA ATRP mechanism and the SET-LRP mechanism. The SET-LRP mechanism assumes that Cu^0 is the major activator of alkyl halides (green dashed line) and that disproportionation (blue dashed line) is the dominant fate for Cu^I complexes. SARA ATRP (red solid lines) assumes that Cu^I is the major activator of alkyl halides and that Cu^I species predominantly activate alkyl halides rather than disproportionate (reprinted with permission from ref. 72. Copyright 2014 the American Chemical Society).

SARA-ATRP: *Polym. Chem.* **2014**, *5*, 4396-4417.   SET-LRP: *Chem. Rev.* **2009**, *109*, 5069-5119.

eATRP

- ## Electrochemical ATRP
  - ### Reduces Cu(II)
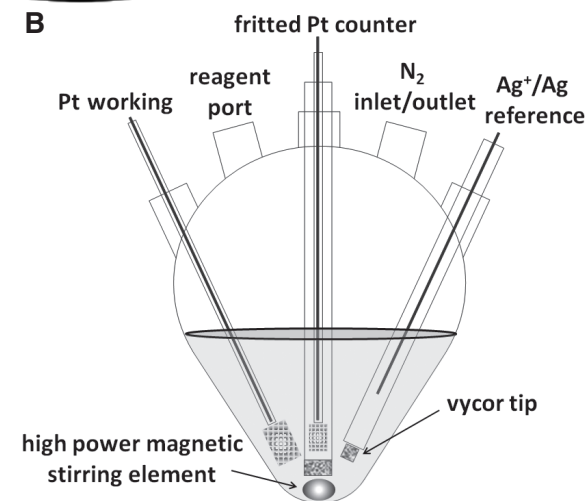
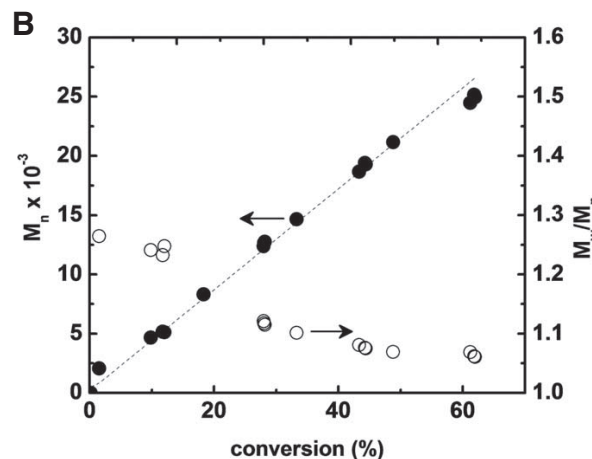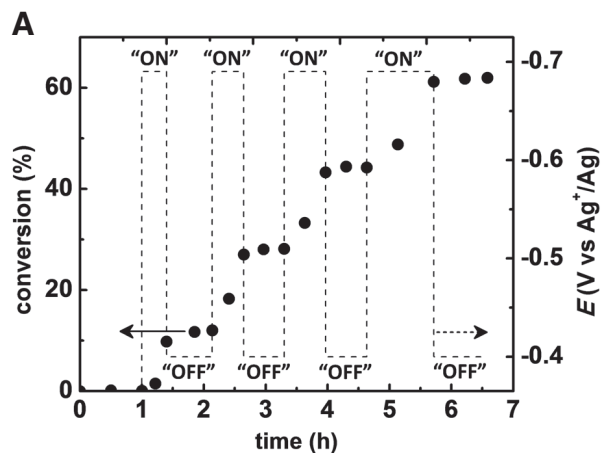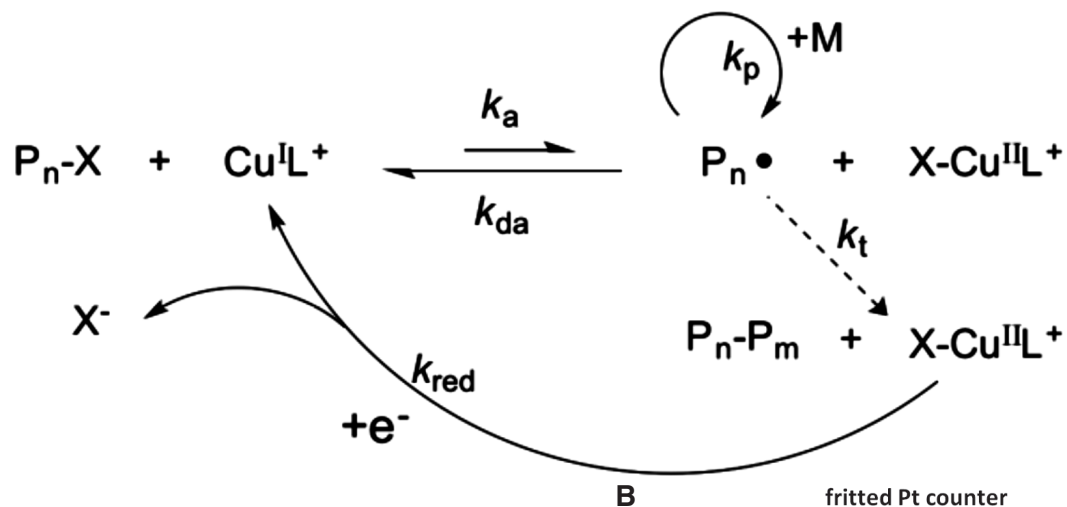**Fig. 4.** (**A**) Conversion (solid circles) and applied potential (dashed line) with respect to time and (**B**) M_n and M_w/M_n with respect to conversion. Toggling between active and dormant states is represented by changes of the E_{app} values between −0.69V and −0.40 V versus Ag⁺/Ag, respectively. Reaction conditions are identical to those stated in Fig. 2.
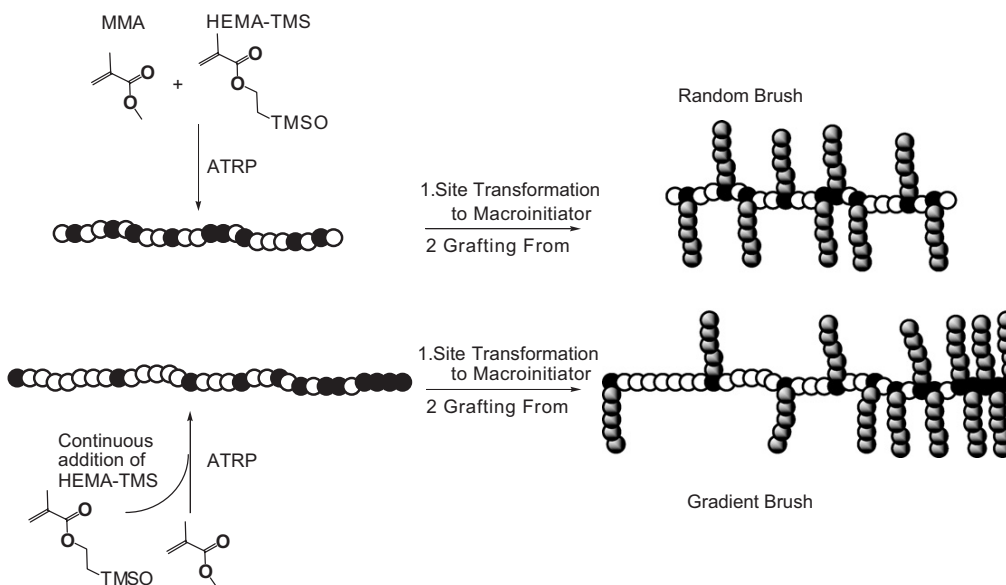
K. Matyjaszewski et al. *Science* **2011**, *332*, 81-84.

Some Interesting Polymers from ATRP

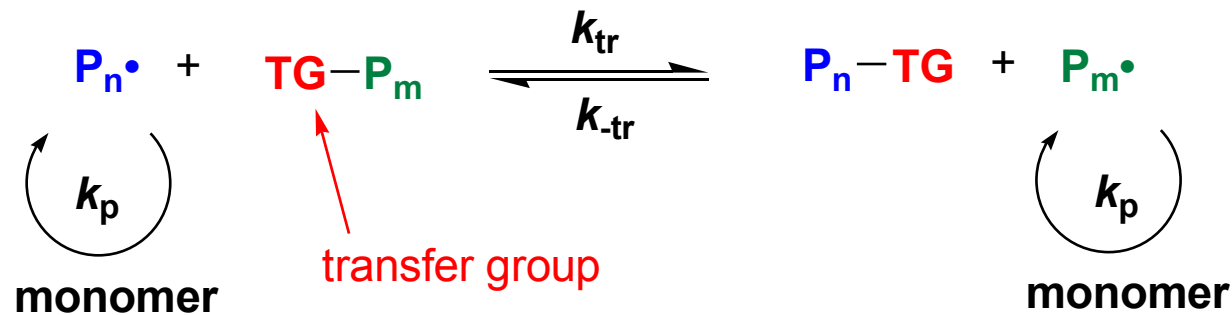- ## Stars
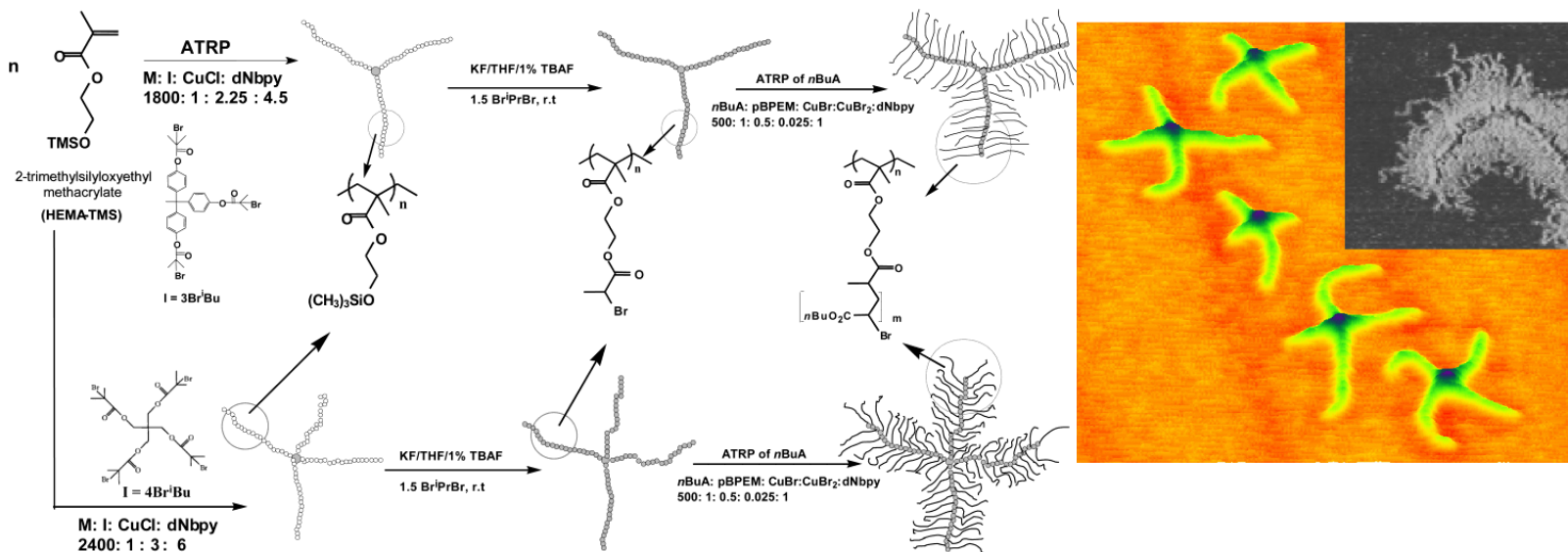
Macromolecules **2003**, *36*, 1843-1849.

- ## Gradients & brushes

Macromolecules **2002**, *35*, 3387-3394.

Degenerate Transfer

- ## Reversible chain transfer

$$P_n\bullet \ + \ TG-P_m \ \underset{k_{-tr}}{\overset{k_{tr}}{\rightleftharpoons}} \ P_n-TG \ + \ P_m\bullet$$

k_p monomer

transfer group

k_p monomer

- ## Examples
  - Iodine-mediated (TG = I atom)
  - Methacrylic macromonomers
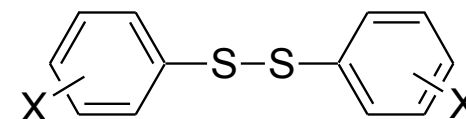 - Thiocarbonylthio (RAFT) polymerization

Iniferters ...1

- *Ini*tiator, trans*fer* agent, *ter*minator

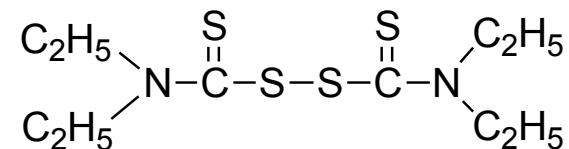Otsu et al. *Makromol. Rapid Commun.*, **1983**, *3*, 127 & 133

- Disulfides
  - High amounts of transfer
  - Examples
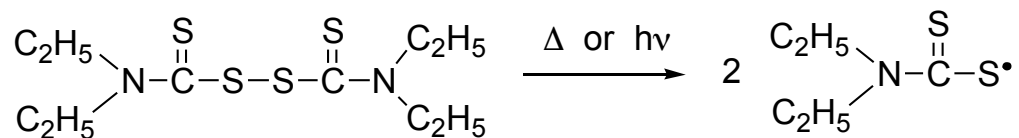   - Diaryl disulfides
    - Dithiuram disulfides (most successful)

- Dithiocarbamyl end groups
  - Thermally stable
  - Photochemically labile

Iniferters ...2

Initiation

Chain Transfer
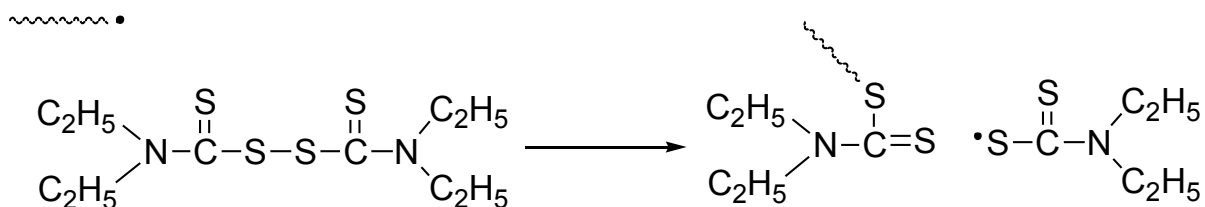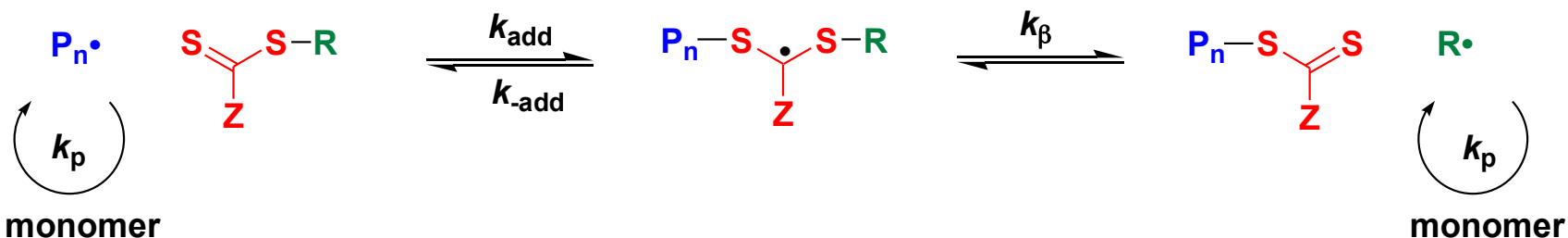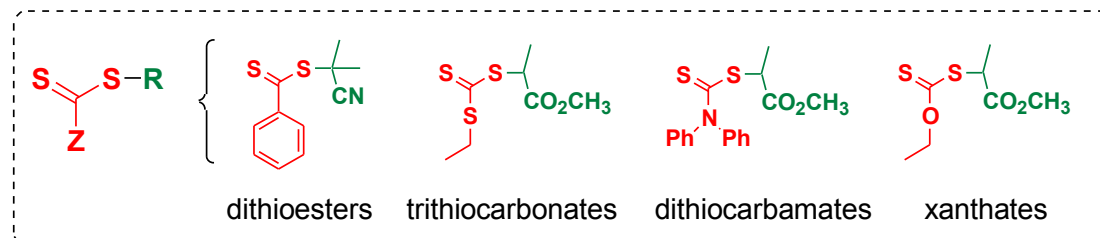

Termination / Reinitiation
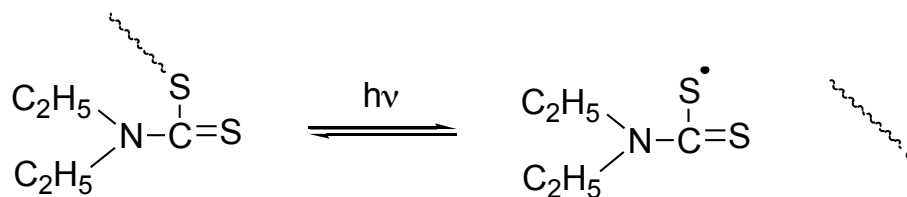
RAFT Polymerization

- Reversible addition-fragmentation chain transfer

Initiation / Chain Transfer

$$I_2 \xrightarrow[\text{monomer}]{\Delta \text{ or } h\nu} P_n\bullet$$
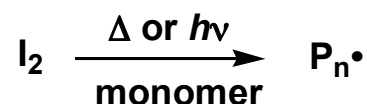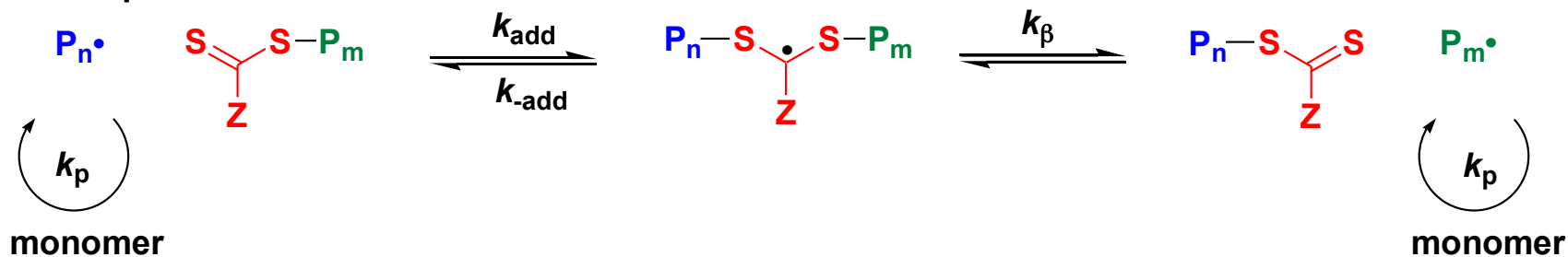
G. Moad, E. Rizzardo, et al., *Macromolecules*, **31**, 5559 (1998)
G. Moad, E. Rizzardo, et al., *Patent WO98/01478* (1998)
S. Z. Zard et al. *Patent WO98/58974* (1998)

Iodine & Methacrylic Macromonomers

- ## Iodine-mediated polymerizations

  - Tatemoto (Eur. Patent 489370A1, **1992**)

  - Matyjaszewski (*Macromolecules*, **1995**, *28*, pp. 2093 and 8051)

$$P_n\bullet \quad + \quad I—P_m \quad \xrightleftharpoons[k_{-tr}]{k_{tr}} \quad P_n—I \quad + \quad P_m\bullet$$

$$k_p \qquad\qquad\qquad\qquad\qquad\qquad k_p$$
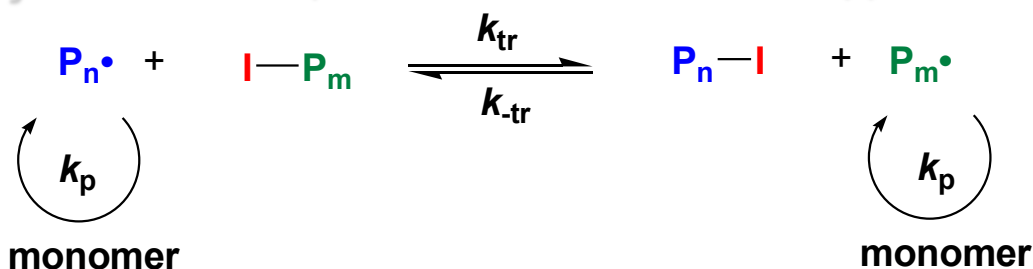
monomer   **monomer**

- Polymerization of vinyl acetate

  - Iovu & Matyjaszewski (*Macromolecules*, **2003**, *35*, 9346)

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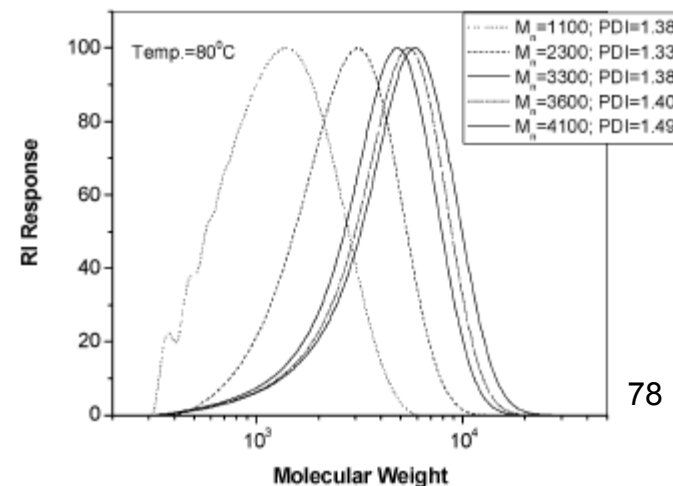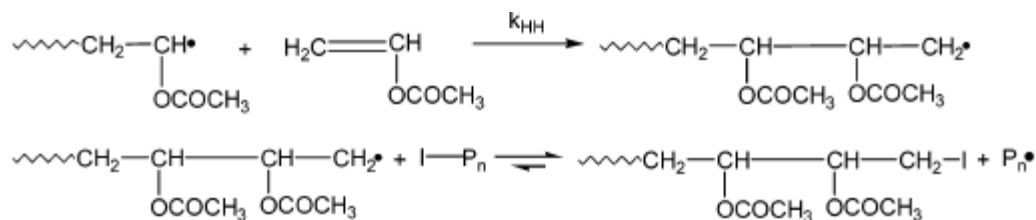
Macromonomer Method

- ## Methacrylate-based macromonomers
  - ### Moad et al. (*Macromolecules*, **1996**, *29*, 7717)

Reaction scheme:

$$P_n\bullet \quad + \quad \text{(macromonomer, } CO_2CH_3\text{)} \quad \underset{k_\beta}{\overset{k_{add}}{\rightleftharpoons}} \quad P_n\!-\!\bullet\!-\!P_m \;(CO_2CH_3) \quad \underset{k_{add}}{\overset{k_\beta}{\rightleftharpoons}} \quad P_n \;(CO_2CH_3) \quad + \quad P_m\bullet$$

k_p monomer (left) k_p monomer (right)
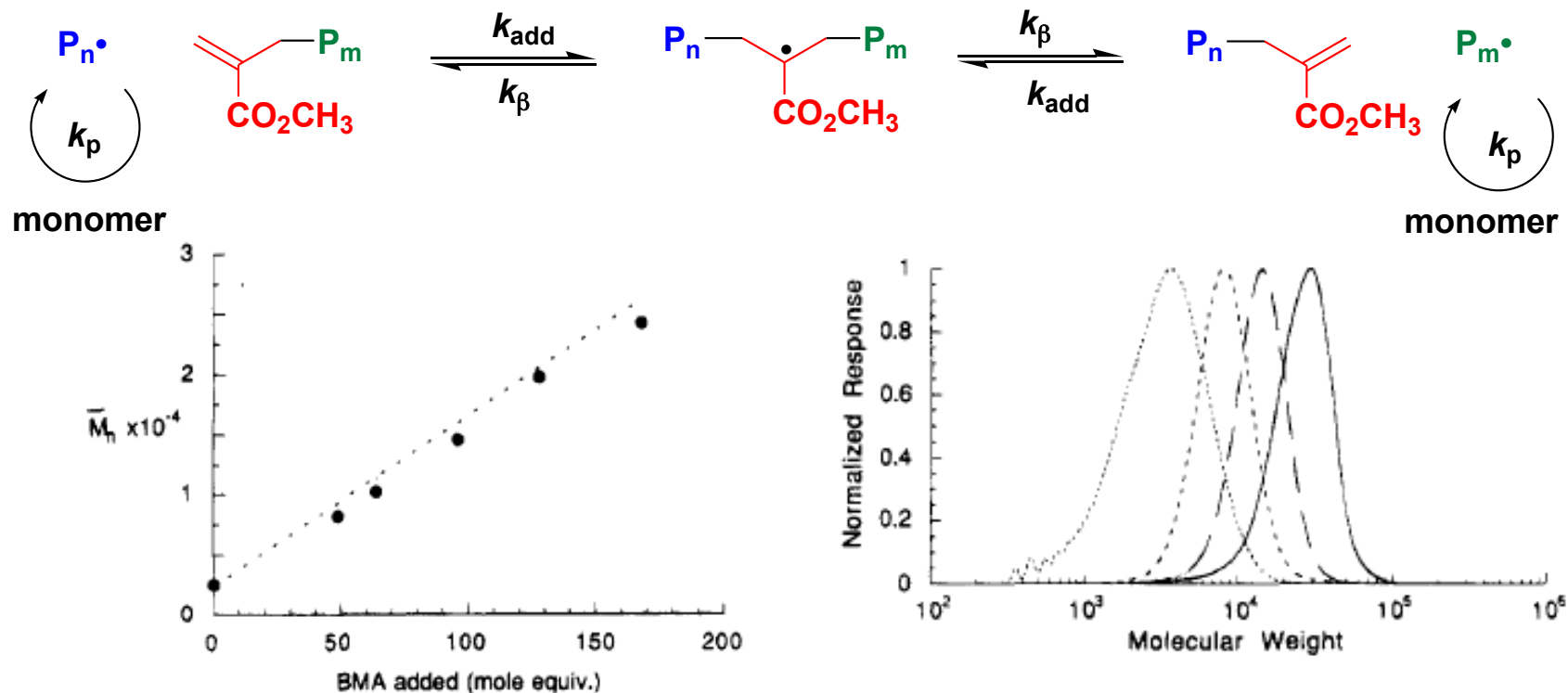
Figure 1. Variation in molecular weight with monomer addition for poly(butyl methacrylate-*block*-methyl methacrylate) synthesis. Data are for the example given in the text and reported in Table 1. Calculated molecular weights (- - -). The initial macromonomer (8.5 g) had $\overline{M}_n = 2300$.

Figure 2. Molecular weight distributions for methyl methacrylate macromonomer (- - -) and for poly(butyl methacrylate-*block*-methyl methacrylate) synthesis after additions of 33.6 (− −), 59.8 (− ·· −), and 88.2 g (−) of BMA. Data are for the example given in the text and reported in Table 1 and Figure 1.

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Macromonomer Mechanism

Moad et al. *Macromolecules*, **1996**, *29*, 7717.

80
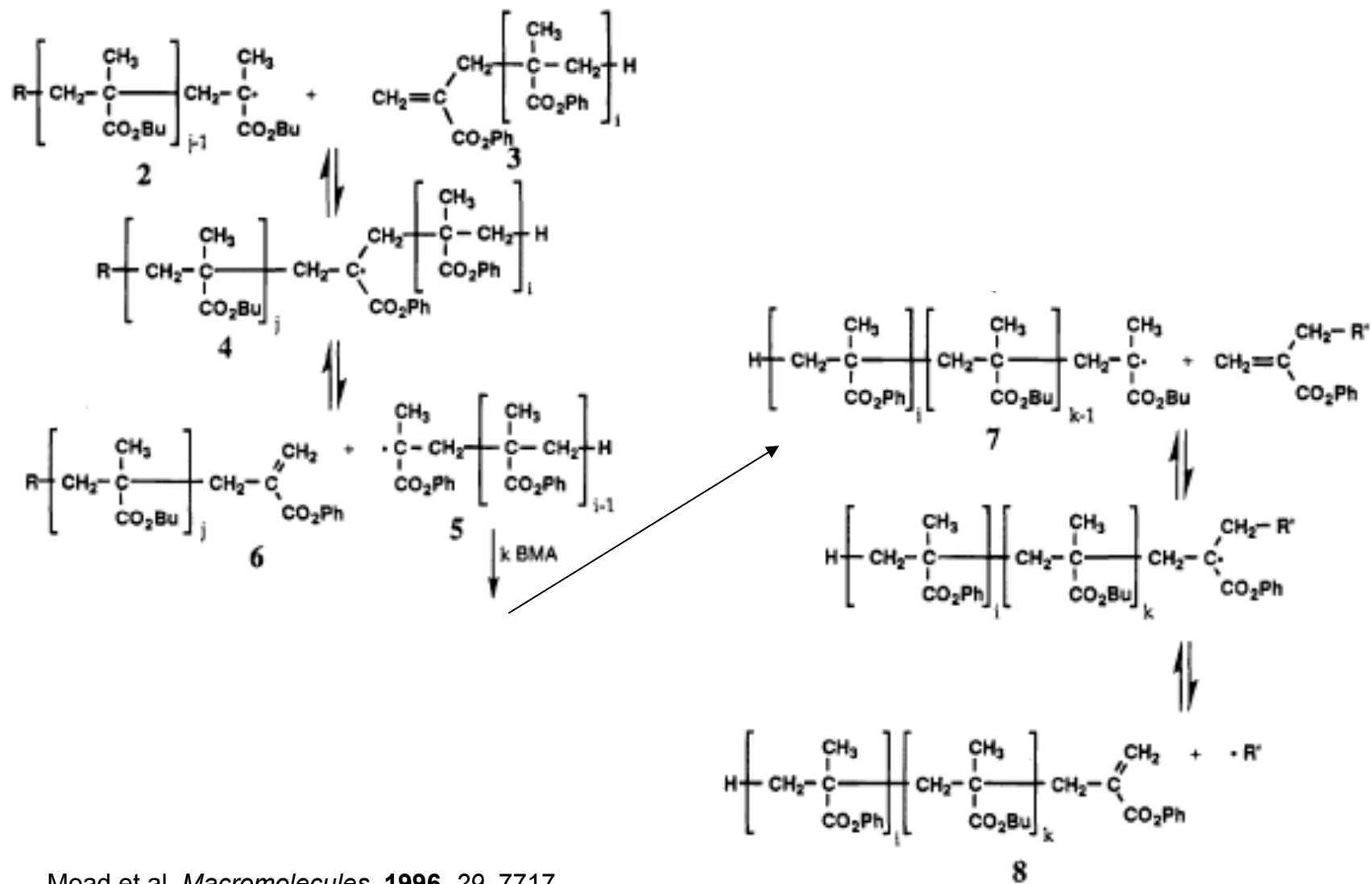
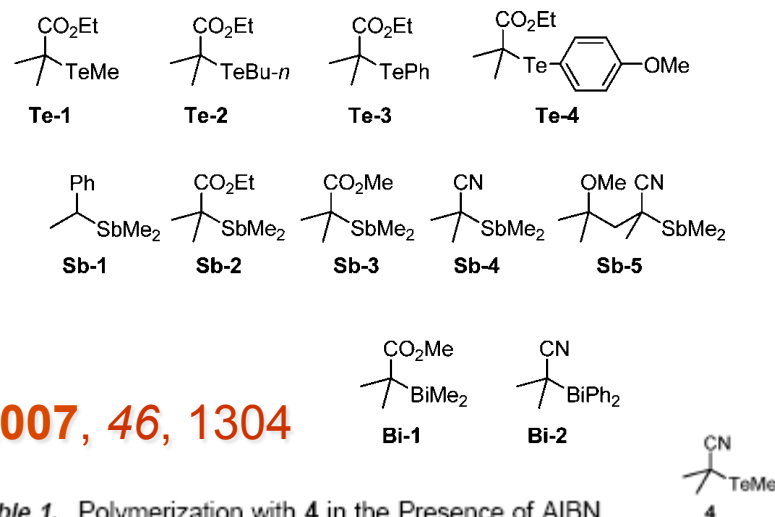# Organoheteroatom-Mediated Polymerization

- ## Organotellurium
  - A. Goto et al. *JACS*, **2003**, *125*, 8720
- ## Organostibine
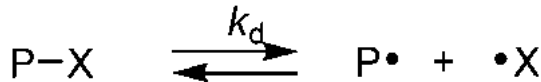 - S. Yamago et al. *JACS*, **2004**, *126*, 13908
- ## Organobismuthin
  - S. Yamago et al. *Angew. Chem. Int. Ed.*, **2007**, *46*, 1304

Two concurrent mechanisms:

(a) Reversible termination (RT) mechanism

$$P{-}X \; \xrightleftharpoons{k_d} \; P{\bullet} \; + \; {\bullet}X$$

(b) Degenerative transfer (DT) mechanism

$$P{-}X \; + \; P'{\bullet} \; \xrightleftharpoons{k_{ex}} \; P{\bullet} \; + \; X{-}P'$$

S. Yamago *Chem. Rev.*, **2009**, *109*, 5051-5068.
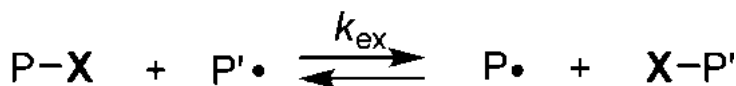
Table 1. Polymerization with **4** in the Presence of AIBN

entry	monomer[a]	method[b]	conditions (°C/h)	yield (%)	M_n[c]	PDI[c]
1	St	A	60/11	94	11300	1.17
2	St	A[d]	60/11	82	4300	1.11
3	St	A[e]	40/23	82	7400	1.21
4	St	B	100/16	96	9200	1.17
5	BA	A	60/4	99	15900	1.19
6	BA	B	100/24	89	10300	1.13
7	MMA	A	60/2	93	11000	1.36
8[f]	MMA	A	60/2	98	9600	1.15
9[f]	MMA	B	80/13	92	9700	1.18
10[g]	NIPAM	A	60/3	99	30600	1.09
11[g]	AN	A	60/6	99	37800	1.16
12[f]	HEMA	A	60/2	99	22300	1.18

[a] St: styrene, BA: *n*-butyl acrylate, MMA: methyl methacrylate, NIPAM: *N*-isopropyl acrylamide, AN: acrylonitrile, HEMA: 2-hydroxyethyl methacrylate. [b] A: A mixture of **4** (1 equiv), AIBN (1 equiv) and monomer (100 equiv) was heated. B: A mixture of **4** (1 equiv) and monomer (100 equiv) was heated.[3] [c] Number-average molecular weight (M_n) and polydispersity index (PDI) were obtained by size exclusion chromatography calibrated by polySt standards for entries 1−4 and 11 and polyMMA standards for others. [d] Two equivalents of **4** was used. [e] V-70 was used instead of AIBN. [f] Dimethyl ditelluride (1 equiv) was added. [g] Reaction was carried out in DMF.

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Cobalt-Mediated Polymerization

- **Organometallic mediated polymerization (OMRP)**
  - Various metals can be used (Ti, V, Fe, Os, Mo, Cr) but most successful is Co
  - Co-mediated polymerization mechanism depends on conditions
    - Degenerate transfer (DT) if high radical conc.
    - Reversible-deactivation (RD) if low radical conc.
  - Largely works for vinyl acetate & acrylates
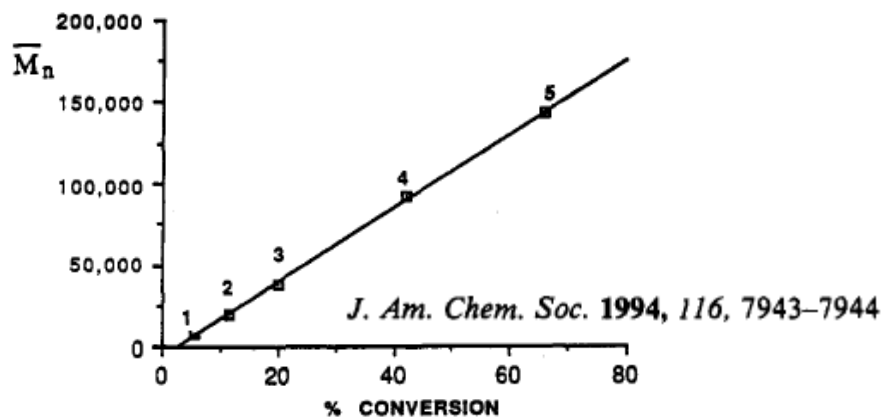   - Ti okay for MMA and derivative

J. Am. Chem. Soc. **1994**, *116*, 7943–7944

Figure 1. Number average molecular weight of PMA versus percent of monomer conversion that results from reaction of (TMP)Co–neopentyl and methyl acrylate (60 °C. benzene: [(TMP)Co–neopentyl]ᵢ = 1.0 × 10⁻³ M; [MA]ᵢ = 2.5 M). Molecular weights of PMA were determined relative to polystyrene standards. (1) $\bar{M}_w/\bar{M}_n$ = 1.10; (2) $\bar{M}_w/\bar{M}_n$ = 1.16; (3) $\bar{M}_w/\bar{M}_n$ = 1.21; (4) $\bar{M}_w/\bar{M}_n$ = 1.17; (5) $\bar{M}_w/\bar{M}_n$ = 1.21.

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